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Surface Chemistry, Friction, and Wear Properties of Untreated and Laser-Annealed Surfaces of Pulsed-Laser-Deposited WS_2 Coatings

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SUMMARY

An investigation was conducted to examine the surface chemistry, friction, and wear behavior of untreated and annealed tungsten disulfide (WS_2) coatings in sliding contact with a 6-mm-diameter 440C stainless-steel ball. The WS_2 coatings and annealing were performed using the pulsed-laser-deposition technique.

All sliding friction experiments were conducted with a load of 0.98 N (100 g), an average Hertzian contact pressure of 0.44 GPa, and a constant rotating speed of 120 rpm. The sliding velocity ranged from 31 to 107 mm/s because of the range of wear track radii involved in the experiments. The experiment was performed at room temperature in three environments: ultrahigh vacuum (vacuum pressure, 7×10^{-7} Pa), dry nitrogen (relative humidity, <1 percent), and humid air (relative humidity, 15 to 40 percent). Analytical techniques, including scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX), x-ray photoelectron spectroscopy (XPS), surface profilometry, and Vickers hardness testing, were used to characterize the tribological surfaces of WS_2 coatings.

The results of the investigation indicate that the laser annealing decreased the wear of a WS_2 coating in an ultrahigh vacuum. The wear rate was reduced by a factor of 30. Thus, the laser annealing increased the wear life and resistance of the WS_2 coating. The annealed WS_2 coating had a low coefficient of friction (<0.1) and a low wear rate (10^{-7} $mm^3/N\cdot m$), both of which are favorable in an ultrahigh vacuum.

INTRODUCTION

While graphite and molybdenum disulfide continue to be the most commonly used inorganic solid lubricants, a number of other inorganic compounds were suggested for special applications, particularly at high temperatures (ref. 1).

Tungsten disulfide (WS_2) is a transition metal disulfide and an effective inorganic lubricant in a vacuum. It behaves very similarly to molybdenum disulfide (MoS_2), although it provides significantly better oxidation resistance during heating in air than MoS_2. WS_2 has an advantage of about 100 °C over MoS_2, with respect to oxidation resistance and thermal stability (refs. 1 and 2).

This present investigation was conducted to examine the friction and wear behavior of untreated and laser-annealed surfaces of the pulsed-laser-deposited WS_2 coatings and to determine the effect of laser annealing on their tribological properties. Unidirectional sliding experiments were conducted with the WS_2 coatings deposited on 440C stainless-steel disks in contact with 6-mm-diameter 440C stainless-steel balls in three environments: ultrahigh vacuum, dry nitrogen, and humid air.

MATERIALS

The WS_2 coatings had a mean surface roughness of 359 nm rms and were deposited on 440C stainless-steel disk substrates. The coatings were produced at room temperature using a pulsed laser beam with a 2- by 4-mm focused spot at 220 mJ/pulse and a 50-Hz pulse rate with KrF gas (248 nm) and a WS_2 target. The thickness of WS_2 coatings was approximately 1 μm. The annealing was performed by impacting a pulsed laser

beam at 38 mJ/cm^2 for 6 min and at a 10-Hz pulse rate, using KrF gas (248 nm). The annealed WS_2 coating surface had a roughness of 285 nm rms.

EXPERIMENT

Characterization

Analytical techniques were used to characterize the tribological surfaces of WS_2 coatings: SEM, to determine the morphology of the wear-surface and wear-debris particles; EDX, to analyze the composition of the wear debris particles, scars, and tracks; XPS, to characterize surface chemistry; surface profilometry, to determine the surface morphology, roughness, and wear of the coatings; and Vickers hardness testing, to determine microhardness of the disk and ball specimens.

Apparatus

Figure 1 shows a vacuum friction apparatus. The apparatus consists of a ball-on-disk assembly mounted in an ultrahigh vacuum chamber, a drive system, and a friction-force measuring system. All components within the vacuum chamber are compatible with oxidizing, inert, and reducing gases.

The specimens of the vacuum friction apparatus are a 19-mm-diameter (5-mm-thick) flat disk and a 6-mm-diameter ball specimen, as shown in the insert (Detail) of figure 1. The disk specimen is mounted on a shaft driven by a gear motor, which is connected to a rotary feedthrough with a ferrofluidic seal. The drive assembly provides rotation at various speeds, which are regulated by a dc motor controller.

For this study, all experiments were performed at a constant rotating speed of 120 rpm. During disk rotation, the ball slid on a constant-diameter wear track located on the disk. The friction force measuring system assembly permitted rotation at various track diameters ranging from 5 to 17 mm, which produced sliding velocities ranging from 31 to 107 mm/s, respectively.

The ball specimen was mounted in a holder attached to one end of a stainless-steel beam. The beam was supported by the friction force measuring system assembly, which was bearing-mounted. The bearing mounting permitted deadweight loading of the ball against the disk surface.

Horizontal movement of the ball, that is, with the disk as it rotated, was restrained by the beam acting as a bending spring. The displacement of the ball was continuously monitored with a linear variable differential transformer during the experiments. The friction force could continuously be recorded in a computerized data acquisition system during friction experiments. A friction force as low as 1 mN (0.1 g) could be measured.

The vacuum system was evacuated in 12 to 15 hr without bakeout to a pressure in the 10^{-7}-Pa range using a turbomolecular vacuum pump and an oil-sealed mechanical pump. Pressure was measured by a nude ionization gage. Residual gas analyses were conducted before, during, and after the friction and wear experiment by using a quadrupole gas analyzer.

Friction and Wear Experiments

Sliding friction experiments were conducted in the chamber shown in figure 1. Before each experiment, the as-received ball specimen was ultrasonically rinsed in an ethanol bath. The ball specimen was then dried in a vacuum desiccator at a pressure of 70 Pa for 20 min at room temperature. The cleaned, dry ball and the as-received WS_2 disk specimen were positioned in the vacuum chamber (fig. 1).

For experiments in an ultrahigh vacuum, the system was evacuated to 7×10^{-7} Pa or better and maintained at this pressure. For experiments in dry nitrogen, the entire vacuum chamber was filled with dry nitrogen at a relative humidity of less than 1 percent; nitrogen gas was admitted through an inlet valve into the system (fig. 1) and maintained at that condition during the entire sliding friction experiment. For experiments in humid air, the vacuum chamber was conditioned in laboratory air at a relative humidity of 40 percent or less during the entire sliding friction experiment.

After the system was conditioned to the desired environment, the pin and disk specimen surfaces were brought into contact and loaded. Afterward, unidirectional, rotating sliding friction experiments were performed in humid air at a relative humidity of 15 to 40 percent; in dry nitrogen, at a relative humidity of less than 1 percent; or in an ultrahigh vacuum at a vacuum pressure of 7×10^{-7} Pa or less. All sliding friction experiments were conducted with a load of 0.98 N (100 g), an average Hertzian contact pressure of 0.44 GPa, and a constant rotating speed of 120 rpm. The sliding velocity ranged from 31 to 107 mm/s because of the range of wear

track radii involved in the experiments. As the disk rotated, the ball scribed a circular wear track on the flat surface of the disk. In each experiment, a new surface of the ball specimen was used.

Wear volumes of the flat disk specimens were obtained from stylus tracing across the wear tracks of at least four locations. The average cross-sectional area of the wear track was then multiplied by the wear track length, which was computed from the diameter of the track at its center to determine the wear volume. Since many of the ball-on-disk or pin-on-disk results were reported using the average specific wear rate or the dimensional wear coefficient expressed in $mm^3/N \cdot m$, an attempt was made to estimate average specific wear rates for WS_2 coatings. The calculated specific wear rate value in this case, being an average, changed with the number of passes completed. Simple compaction of the WS_2 coating under load may primarily occur during running in. Afterwards, a burnishing wear could dominate the overall wear rate. Therefore, the average specific wear rate for a material such as the WS_2 coating should be viewed with caution.

Disk Substrates and Ball Specimens

The average surface roughness of the 440C stainless-steel disk substrates, as measured with a surface profilometer, was 12 nm rms. Each roughness value was the average of 20 measurements. The average Vickers microhardness number measured for the uncoated 440C stainless-steel disks was 695 (i.e., 6.8 GPa) over the load range from 0.49 to 4.9 N.

The 6-mm-diameter ball specimens were 440C stainless-steel balls. The average surface roughness of the as-received 440C stainless-steel balls, measured with a surface profilometer, was 8 nm rms. Each roughness value was the average of 20 measurements. The average Vickers microhardness for 440C stainless-steel balls was approximately 25 percent greater than that for uncoated stainless-steel disks over the load range from 0.49 to 4.9 N.

RESULTS AND DISCUSSION

X-ray Photoelectron Spectroscopy Analysis

Figure 2 presents XPS survey spectra of the untreated and laser-annealed WS_2 coatings taken with Mg K_α radiation. The major elements present in both coatings were W, S, O, and C. A small amount of N was present on the surface of the untreated specimen. XPS depth profiles showing the concentrations of the major elements as a function of the depth from the surface were obtained from both films. The N on the untreated coating disappeared immediately upon sputtering and so was not included in the profiles. The profiles were done by recording high-resolution spectra of the W_{4f}, S_{2p}, O_{1s}, and C_{1s} regions, sputtering 50 s, and repeating the procedure until the total sputter time reached 300 s. Under the conditions used, the sputter etch rate was 0.021 nm/s as calibrated on a Ta_2O_5 standard. Quantification of the profiles was done using sensitivity factors supplied by the instrument manufacturer. No standards were run.

The major difference in the XPS analyses of the two films is evident from the depth profiles shown in figure 3. In the unannealed coating, there was almost no C or O below the depth of 3 nm. On the other hand, in the laser-annealed coating, C and especially O persisted throughout the profile. The S concentration in the laser-annealed coating was correspondingly less than in the untreated coating, although the W concentrations were about the same.

The high-resolution O_{1s} spectra taken after 300-s sputtering confirmed the much greater O concentration in the laser-annealed coating than in the unannealed film (fig. 4). High-resolution S_{2p} spectra from the surface (fig. 5) and from 6 nm deep (fig. 6) showed that the S was present as the sulfide at all levels in both coatings. In particular, any sulfate would give a peak at a much higher binding energy, as indicated on these spectra. The high-resolution W_{4f} spectra were composed of a poorly resolved 7/2 and 5/2 doublet in the 31- to 35-eV range and a $5p_{3/2}$ line around 37 eV (figs. 7 and 8). The published positions of the 7/2 line for several possible W compounds are indicated in figure 7. Each of these would have a corresponding 5/2 and $5p_{3/2}$ component.

In summary of XPS analysis, the surface oxides, represented by the initial high O concentrations in the depth profiles, were 1 to 2 nm deep. To a depth of 6 nm, the untreated coating was relatively uncontaminated WS_2, while the laser-annealed coating contained high levels of O and somewhat less C, which replaced S in the coating. In all cases, the S was present as the sulfide.

Friction Behavior

Figure 9 shows friction traces for the untreated WS_2 coating deposited on a 440C stainless-steel disk in sliding contact with 440C stainless-steel balls obtained in the three different environments: ultrahigh vacuum, dry nitrogen, and humid air. In these figures, the coefficients of friction for WS_2 coatings are plotted as a function of the number of passes. The trends of the coefficient of friction with the number of passes varies with the environment. In general, the coefficient of friction gradually increased with the increasing number of passes in air, while in dry nitrogen, the coefficient of friction decreased with the increasing number of passes. In an ultrahigh vacuum, the coefficients of friction showed considerable scatter, as shown in figure 9(c).

The traces in figure 9 show closely spaced irregularities. In general, the heights of the irregularities in the friction traces that were investigated strongly depended on the environment, and, were, in ascending order: dry nitrogen, humid air, and ultrahigh vacuum.

In air and dry nitrogen, friction traces of the laser-annealed WS_2 coating were similar to those of the untreated WS_2 coating. In ultrahigh vacuum the coefficient of friction for the laser-annealed WS_2 coating was less scattered than that for the untreated one (fig. 10). The heights of irregularity in the friction trace of the laser-annealed WS_2 coating was much smaller than that of the untreated WS_2 coating.

Wear Behavior

The SEM observations indicated that the wear surfaces of the untreated and annealed WS_2 coatings took on a burnished appearance (e.g., fig. 11), regardless of environment. Both coating surfaces exhibited adhesive wear, (i.e., burnishing).

The wear track of the untreated and annealed WS_2 coatings revealed that the sliding action generated a smooth wear surface, fine wear-debris particles, and agglomerated, pasty wear debris (e.g., fig. 12). Thin, layered WS_2 was present on the smooth wear tracks. Most of the wear debris accumulated outside the wear tracks.

The wear scar of 440C stainless-steel balls revealed that the wear scar was generally smooth (e.g., fig. 13), regardless of whether the coatings were untreated or annealed, and of the environment. Thin, smeared wear patches of WS_2 generally covered the smooth wear scars. Smeared tongues of thin, layered, agglomerated wear debris were also present. Most of the loose and smeared wear debris accumulated outside the wear scars.

Wear Life

Sliding wear (endurance) lives of the WS_2 coatings deposited on 440C stainless-steel disks were determined to be the number of passes at which the coefficient of friction rapidly rose to approximately 0.8 in humid air, to 0.15 in dry nitrogen, and to 0.30 in an ultrahigh vacuum. The sliding wear lives are presented in figure 14.

The sliding wear lives varied with the environment, similar to the coefficient of friction. With both untreated and annealed WS_2 coatings, the wear life and resistance of the films were, in ascending order: humid air, ultrahigh vacuum, and dry nitrogen. The wear life of both coatings were around 9000 passes in humid air, while the wear life was greater than 2 million passes in dry nitrogen. In an ultrahigh vacuum, the wear life of the laser-annealed WS_2 coating was 10 times or more greater than that of the untreated one; the wear life of the untreated WS_2 coating was around 50,000 passes, while that of the laser-annealed WS_2 coating was greater than 500,000 passes. Thus, laser annealing greatly increased the sliding wear life of WS_2 coating, especially in an ultrahigh vacuum.

Coefficient of Friction and Wear Rate

Figure 15 presents the steady-state (equilibrium) coefficients of friction and wear rates (dimensional wear coefficient) for the untreated and annealed WS_2 coatings in an ultrahigh vacuum, dry nitrogen, or humid air. Both the steady-state coefficients of friction and wear rates of the WS_2 coatings depended on the environment and, were, in ascending order: dry nitrogen, ultrahigh vacuum, and humid air.

The annealing had an influence on the wear rate of the WS_2 coatings in an ultrahigh vacuum; the wear rate of the untreated WS_2 coating was 30 times greater than that of the annealed one. The coefficient of friction for the annealed surface revealed slightly lower friction and much less erratic behavior than that for the

untreated surface. On the other hand, the annealing did not have much influence on the coefficients of friction and wear rates of WS_2 coatings in dry nitrogen and humid air.

CONCLUDING REMARKS

The surface oxides covered over a pulsed-laser-deposited WS_2 coating surface were 1 to 2 nm deep. To a depth of 6 nm, the untreated coating was relatively uncontaminated WS_2, while the laser-annealed coating contained high levels of oxygen and somewhat less carbon, which replaced sulfur in the coating. In all cases, the sulfur was present as the sulfide.

The laser annealing decreased wear of the WS_2 coating. In the ultrahigh vacuum, the reduction of wear rate by a factor of 30, was accompanied by an increase in the wear life and resistance of the WS_2 coating. The annealed WS_2 coating had a low coefficient of friction (<0.1) and a low wear rate (10^{-7} $mm^3/N \cdot m$), which are a favorable friction and wear behavior in an ultrahigh vacuum.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Kent Eisentraut of Wright Laboratory, Wright Patterson Air Force Base, Ohio for supporting this study and producing the untreated and annealed WS_2 coatings, Ronald E. Miller and Mark Jansen for specimens preparation and experimental setups, and Duane J. Dixon for SEM.

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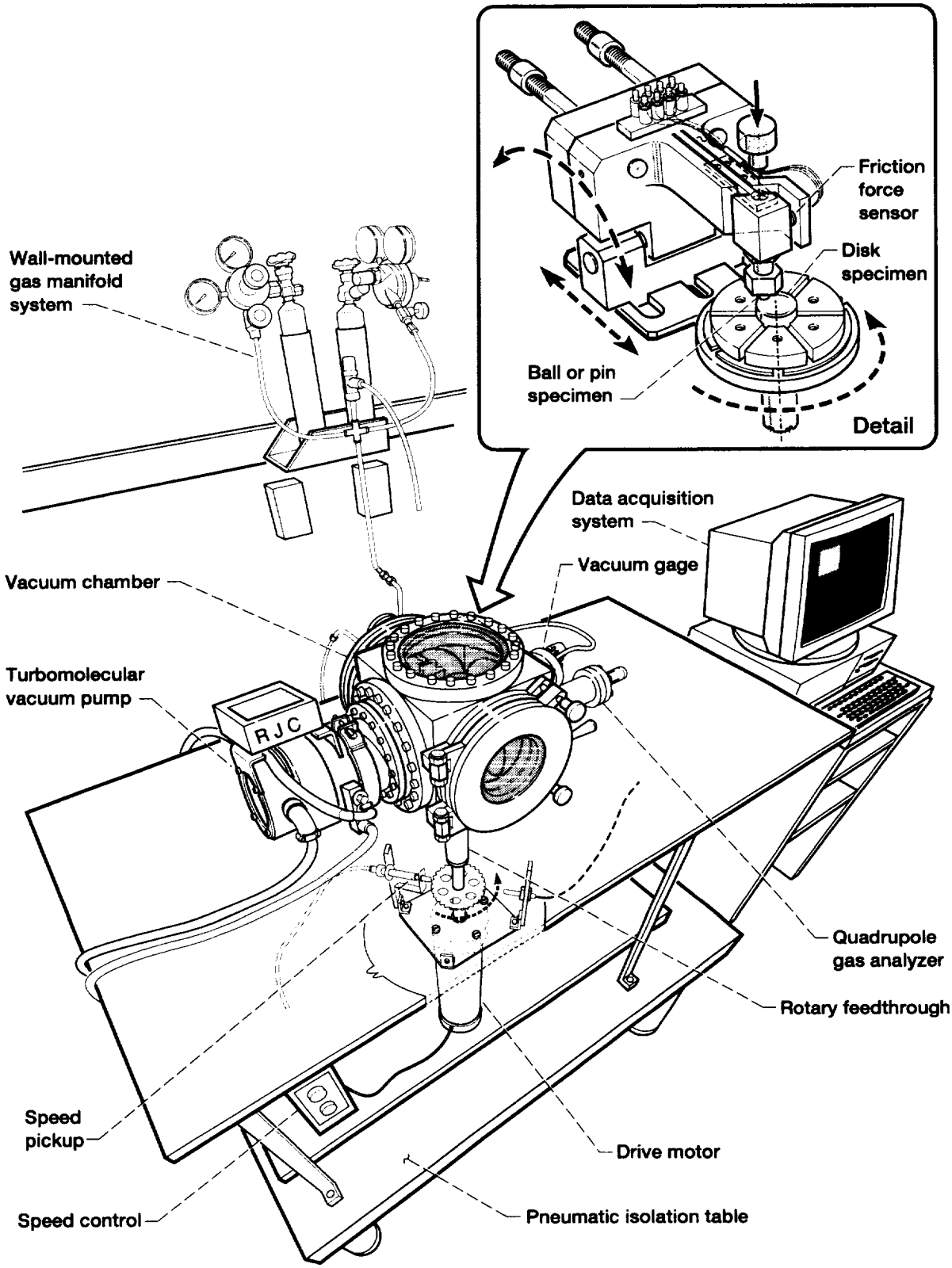

Figure 1.—Vacuum chamber friction and wear apparatus.

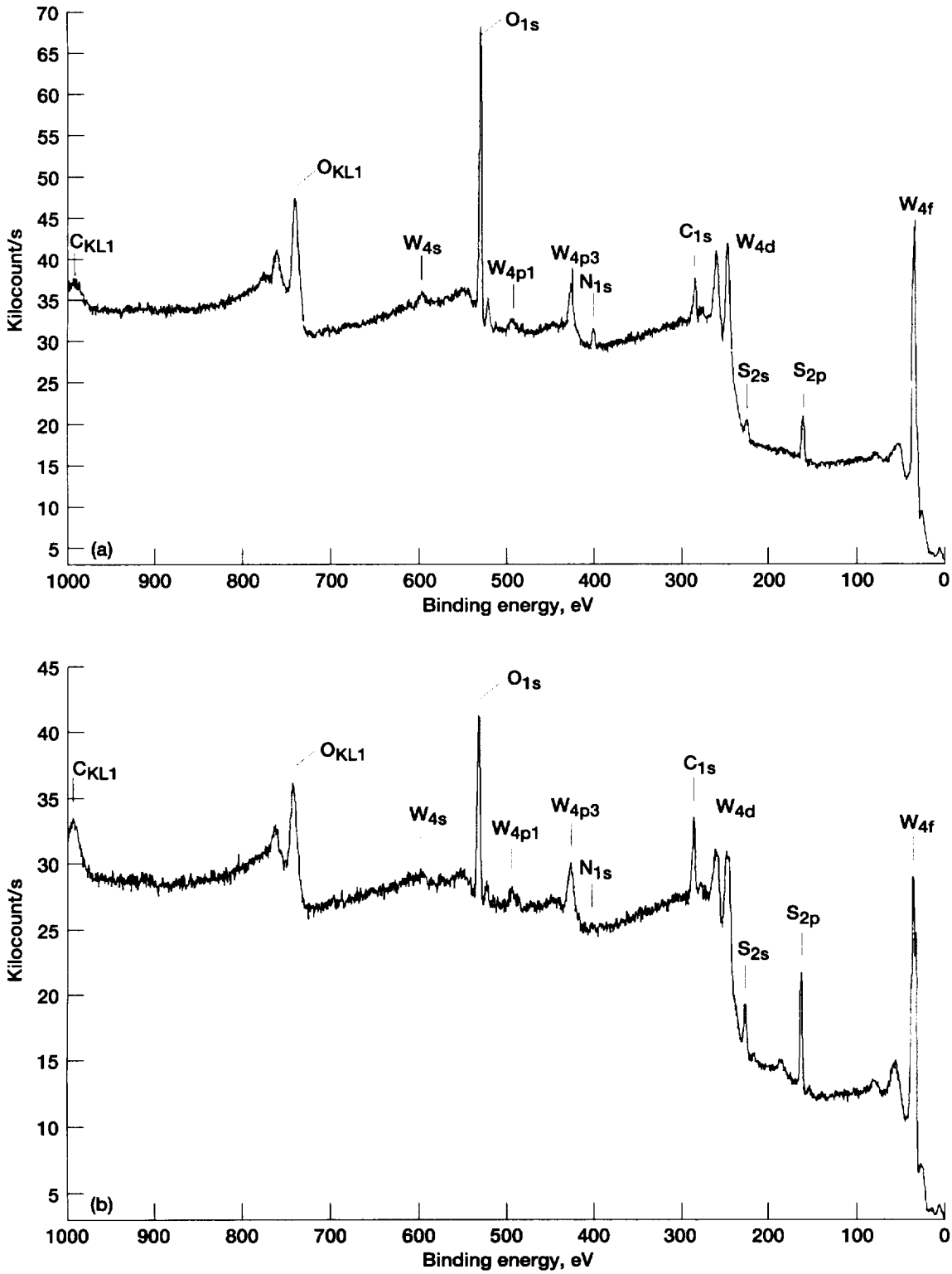

Figure 2.—X-ray photoelectron spectroscopy (XPS) survey spectra of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

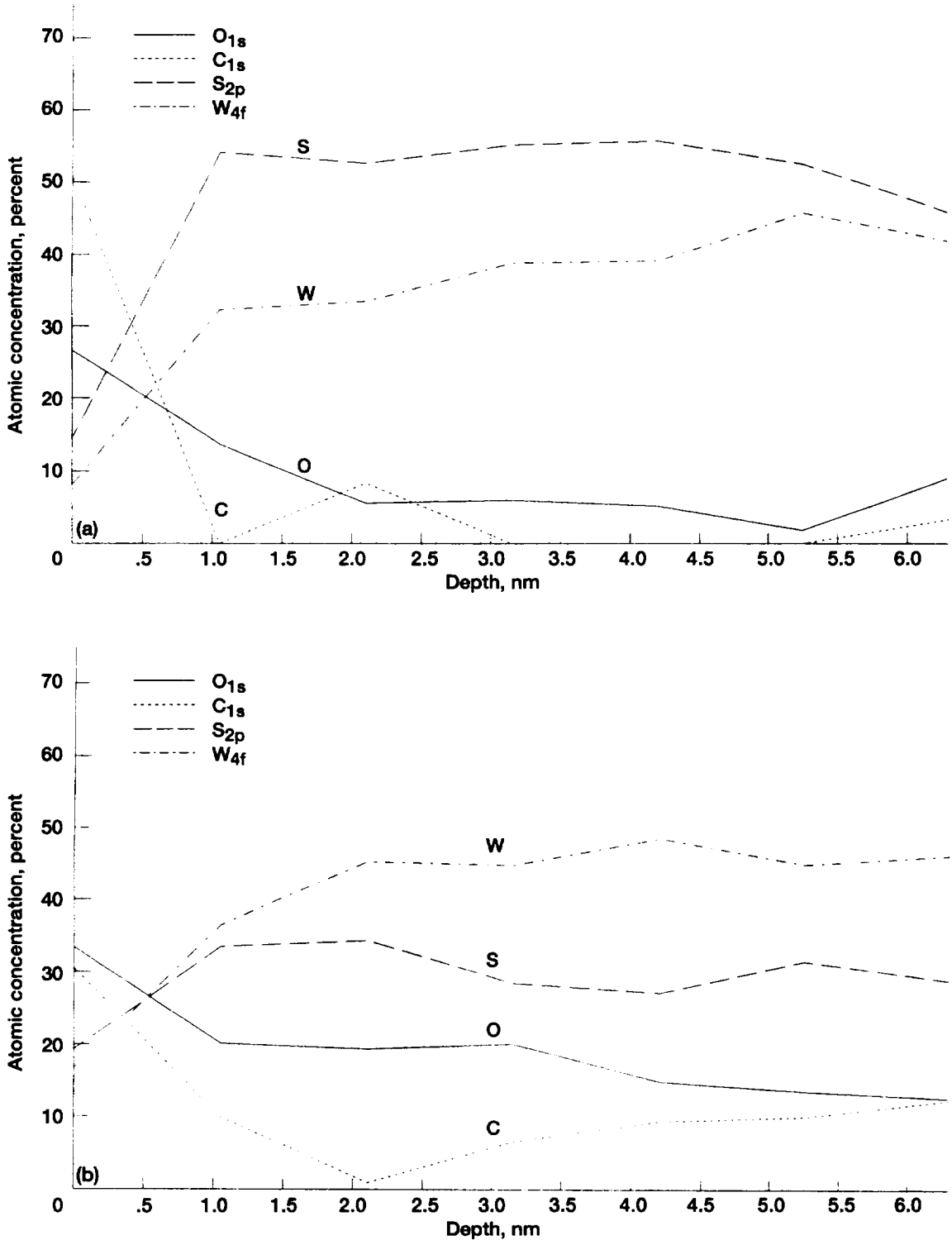

Figure 3.—X-ray photoelectron spectroscopy (XPS) depth profiles of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

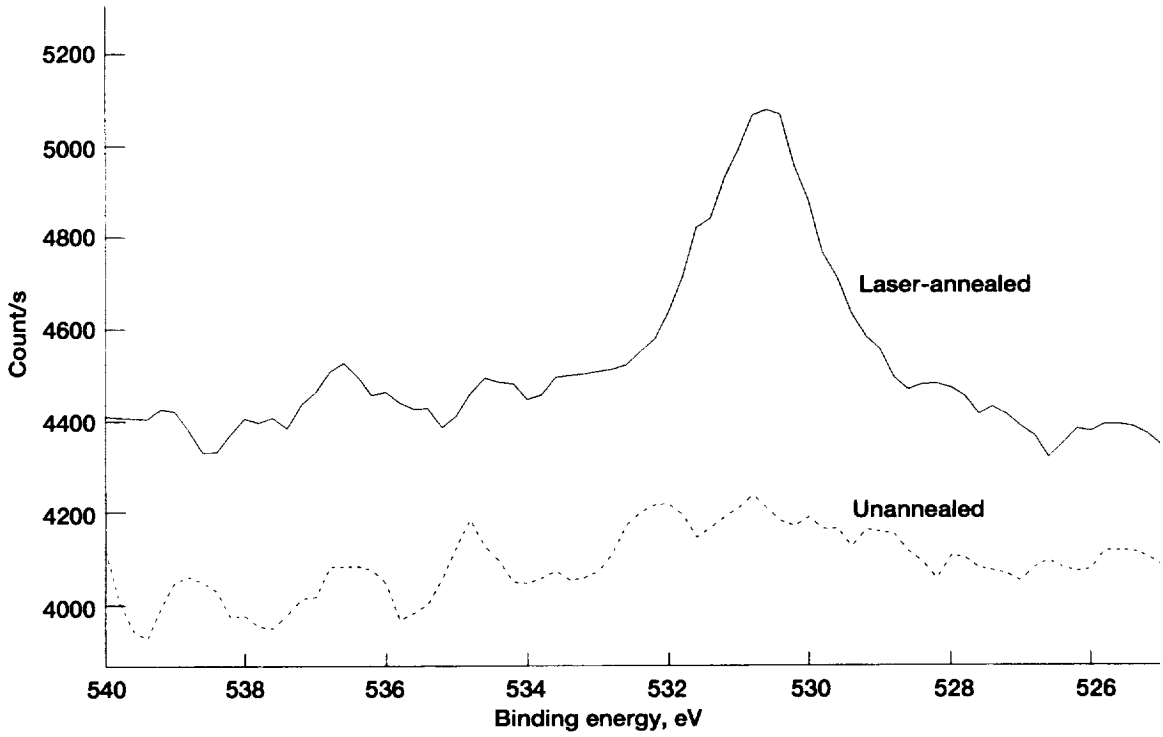

Figure 4.—O_{1s} spectra (at 300 s sputtering) of pulsed-laser-deposited WS_2 coatings.

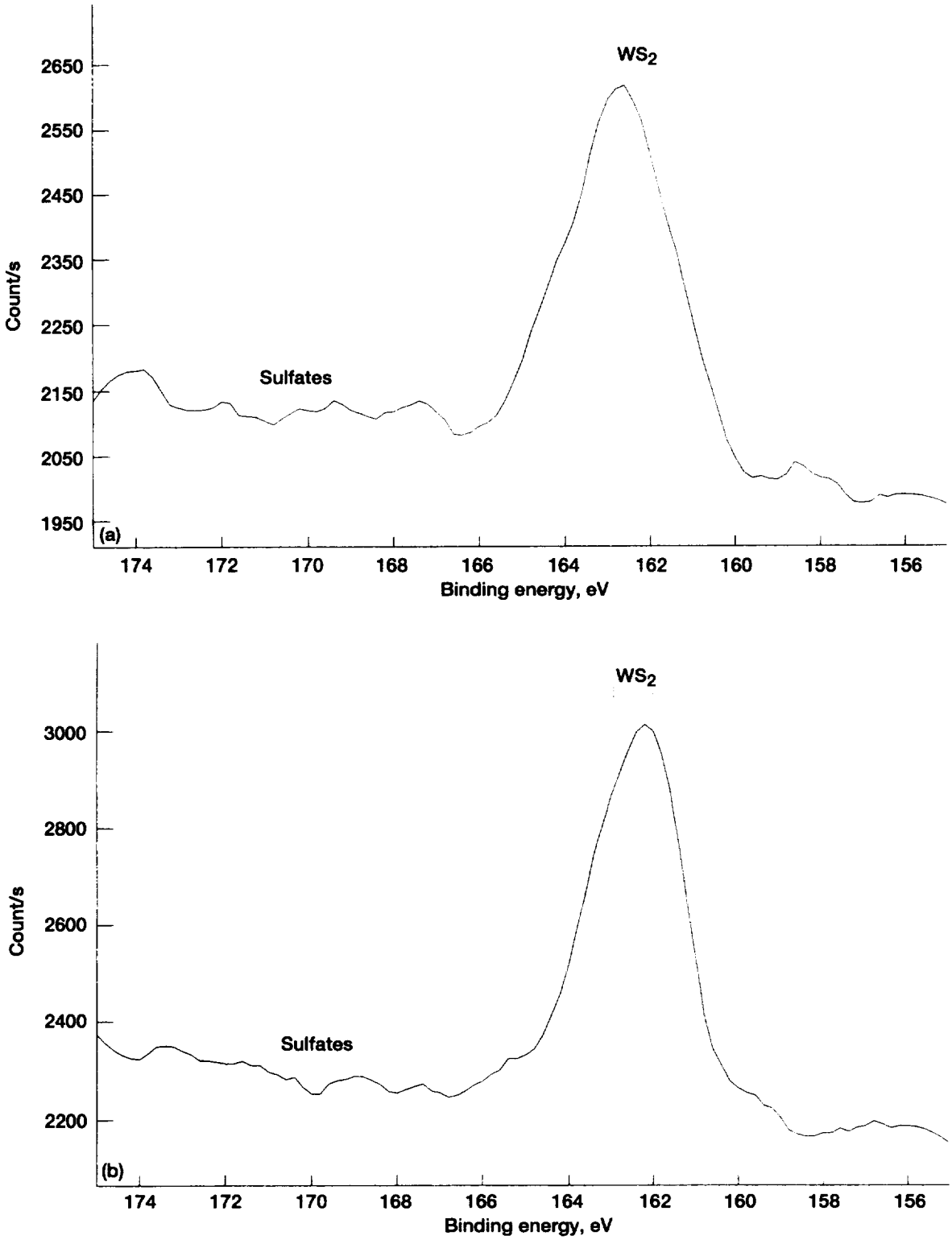

Figure 5.—S_{2p} spectra of surfaces of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

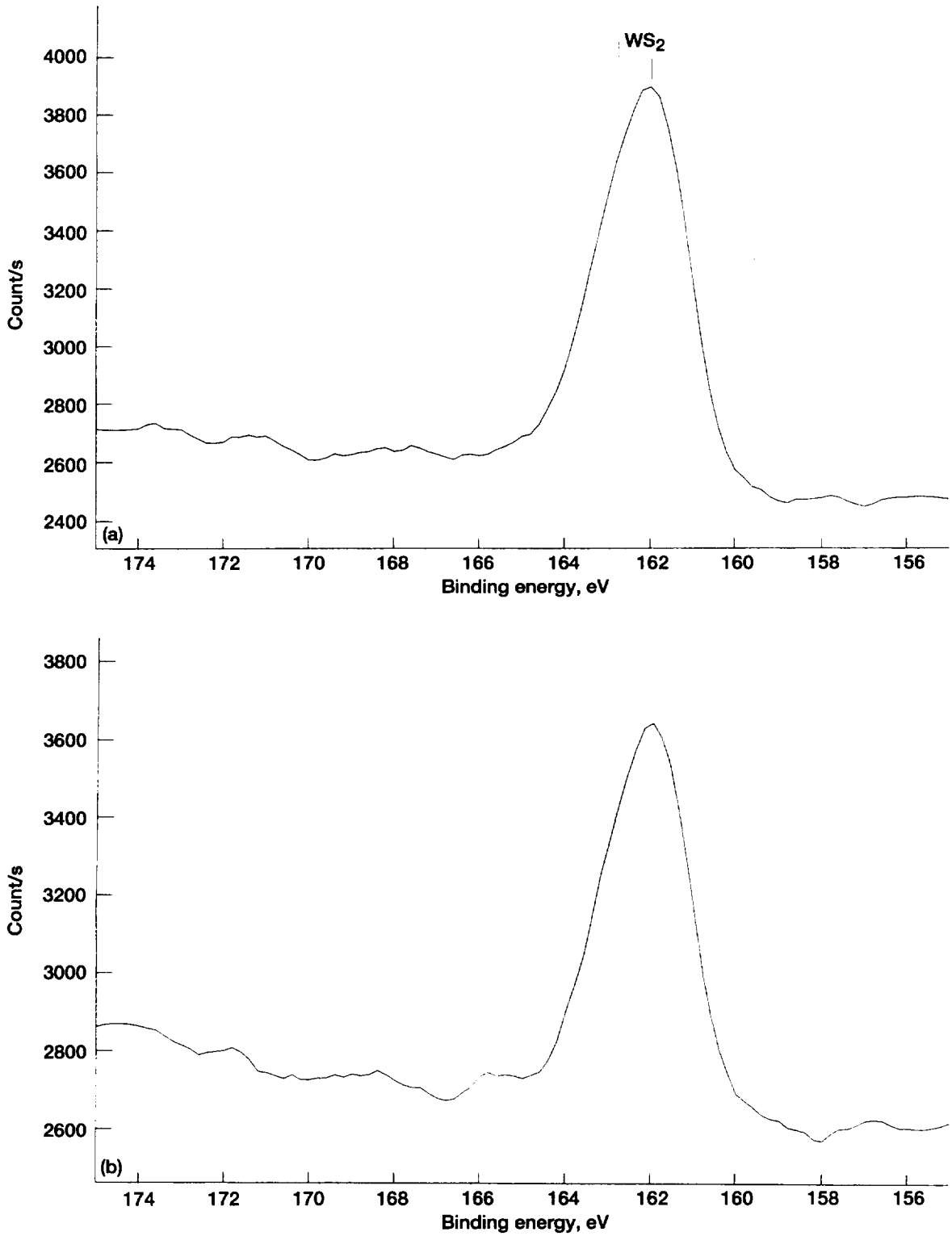

Figure 6.—S_{2p} spectra (at 300-s sputtering) of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

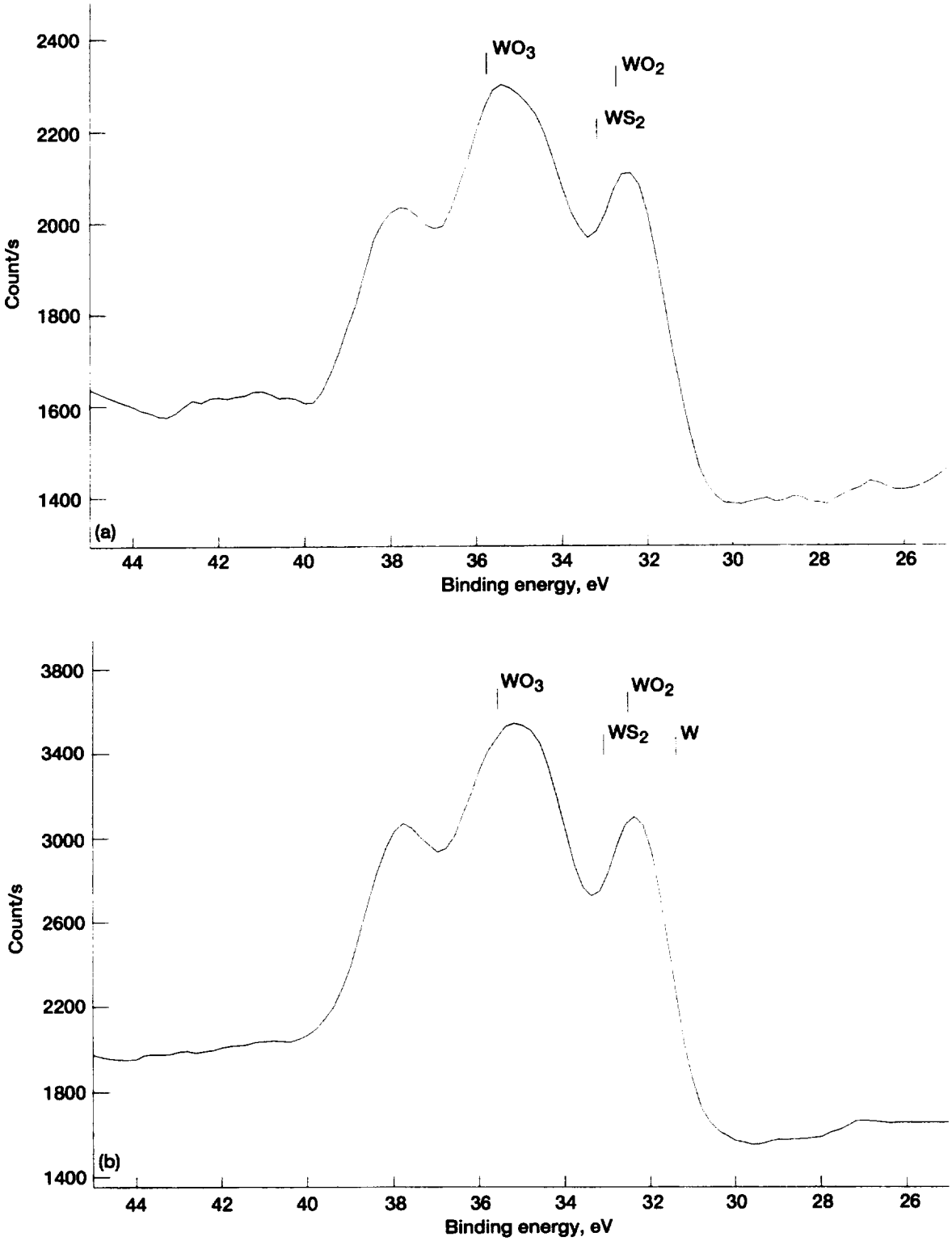

Figure 7.—W_{4f} spectra of surfaces of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

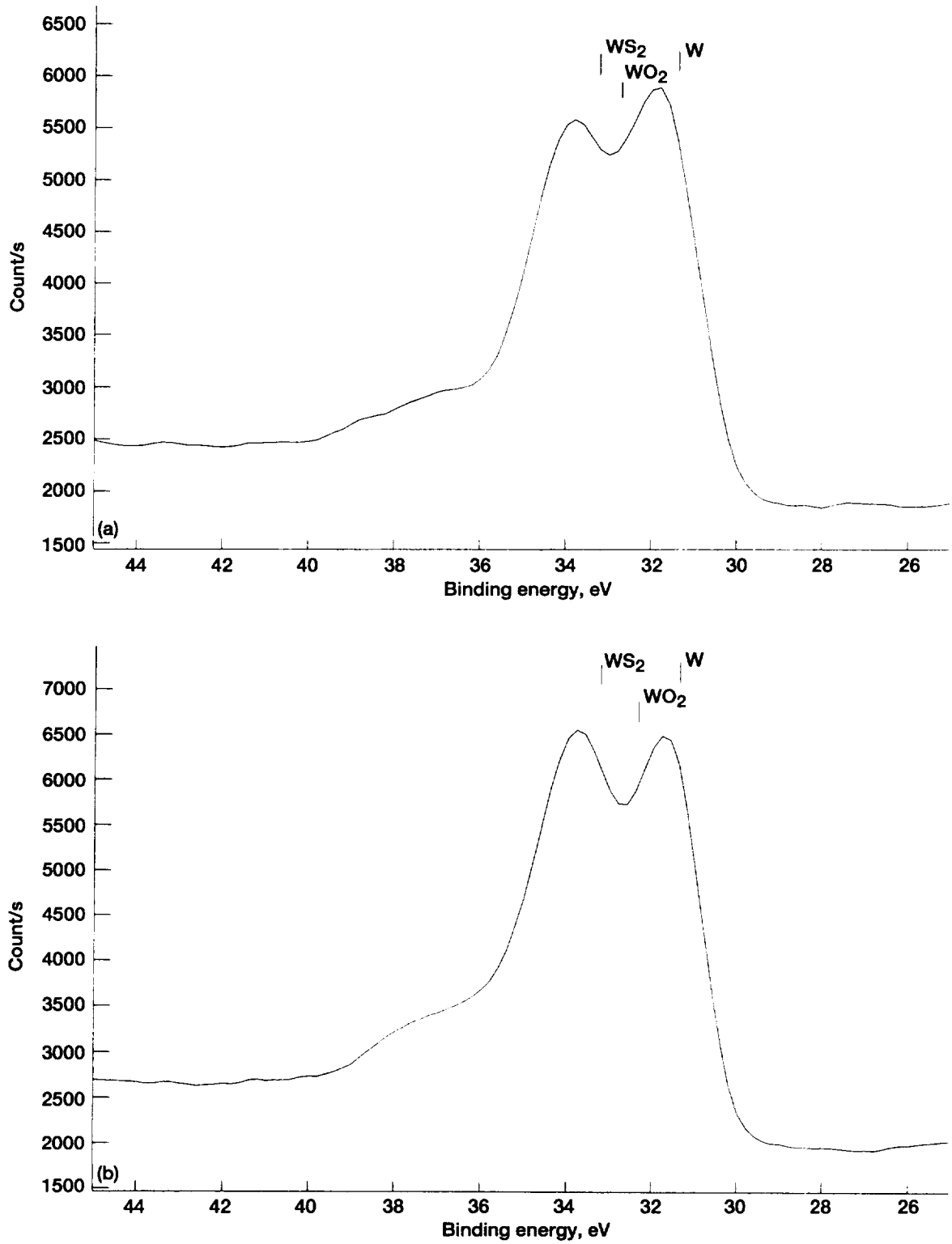

Figure 8.—W_{4f} spectra (at 300-s sputtering) of pulsed-laser-deposited WS_2 coatings. (a) Untreated. (b) Laser-annealed.

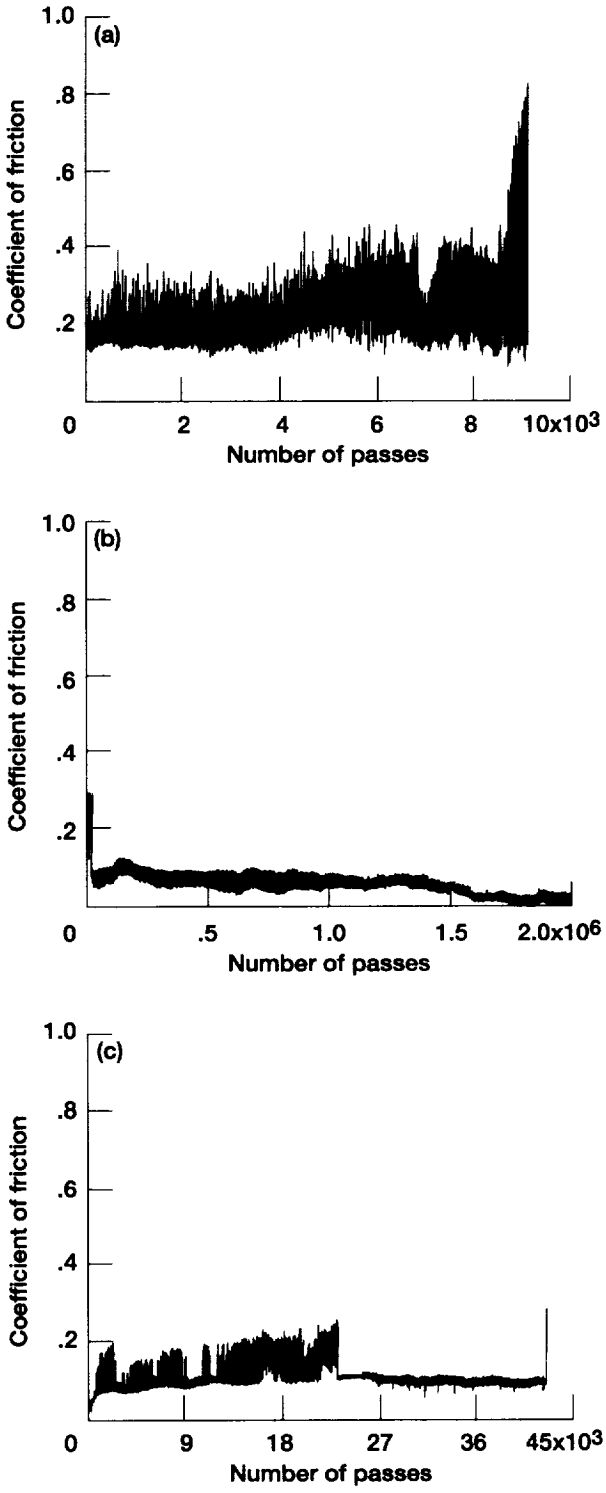

Figure 9.—Friction traces for untreated WS_2 coating in sliding contact with 440C stainless-steel balls in various environments. (a) Humid air. (b) Dry nitrogen. (c) Ultrahigh vacuum.

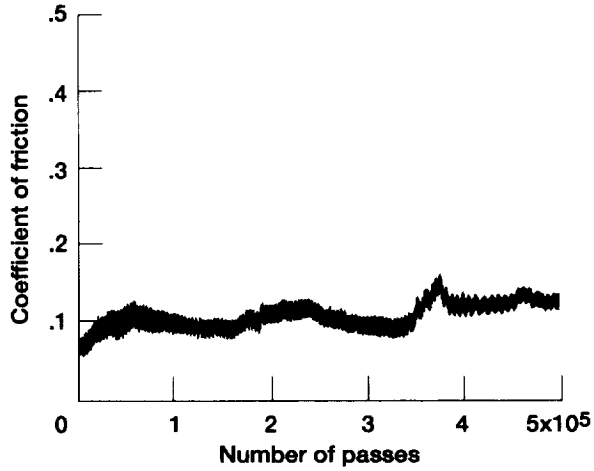

Figure 10.— Friction traces for laser-annealed WS_2 coating in sliding contact with 440C stainless-steel balls in ultrahigh vacuum environment.

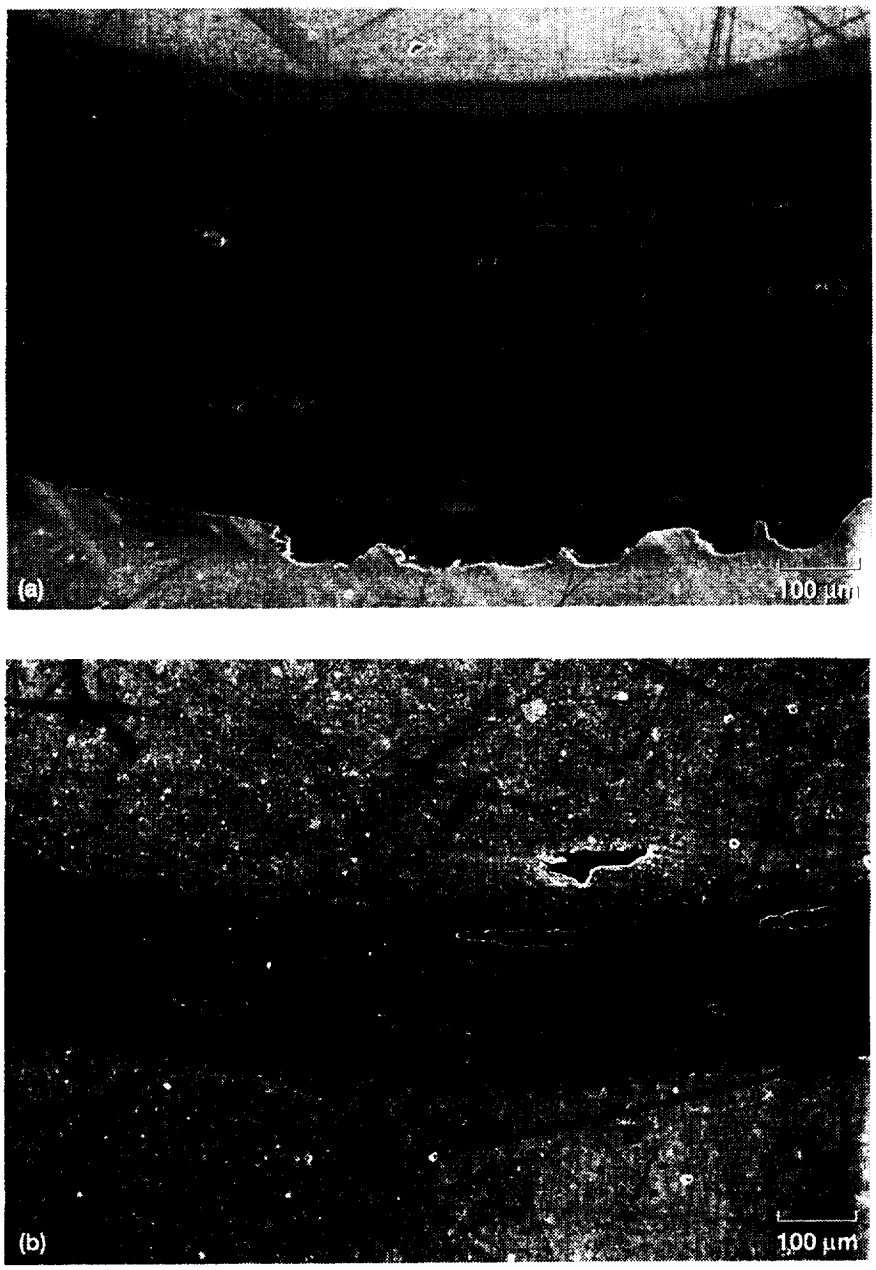

Figure 11.—Wear tracks produced on laser-annealed WS_2 coating after sliding contact. (a) Scanning electron microscopy (SEM) image of wear track and its surroundings at 25 500 passes in air. (b) SEM image of wear track and its surroundings at 2 million passes in dry nitrogen. (c) SEM image of a wear track and its surroundings at 607 990 passes in ultrahigh vacuum.

Figure 11.—Concluded.

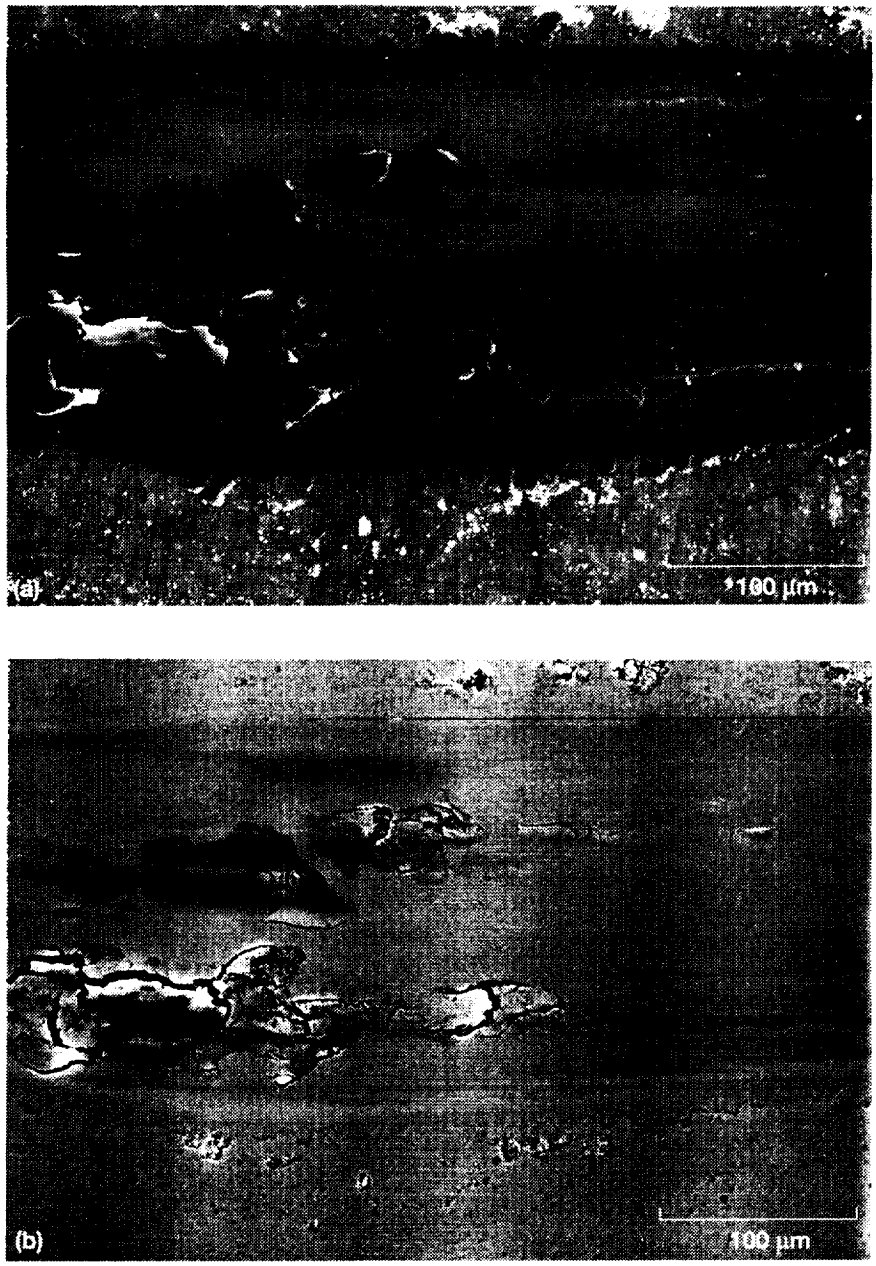

Figure 12.—Wear track produced on laser-annealed WS_2 coating after sliding contact at 607 990 passes in ultrahigh vacuum. (a) Secondary electron image of wear track and its surroundings. (b) Backscatter electron image of wear track and its surroundings.

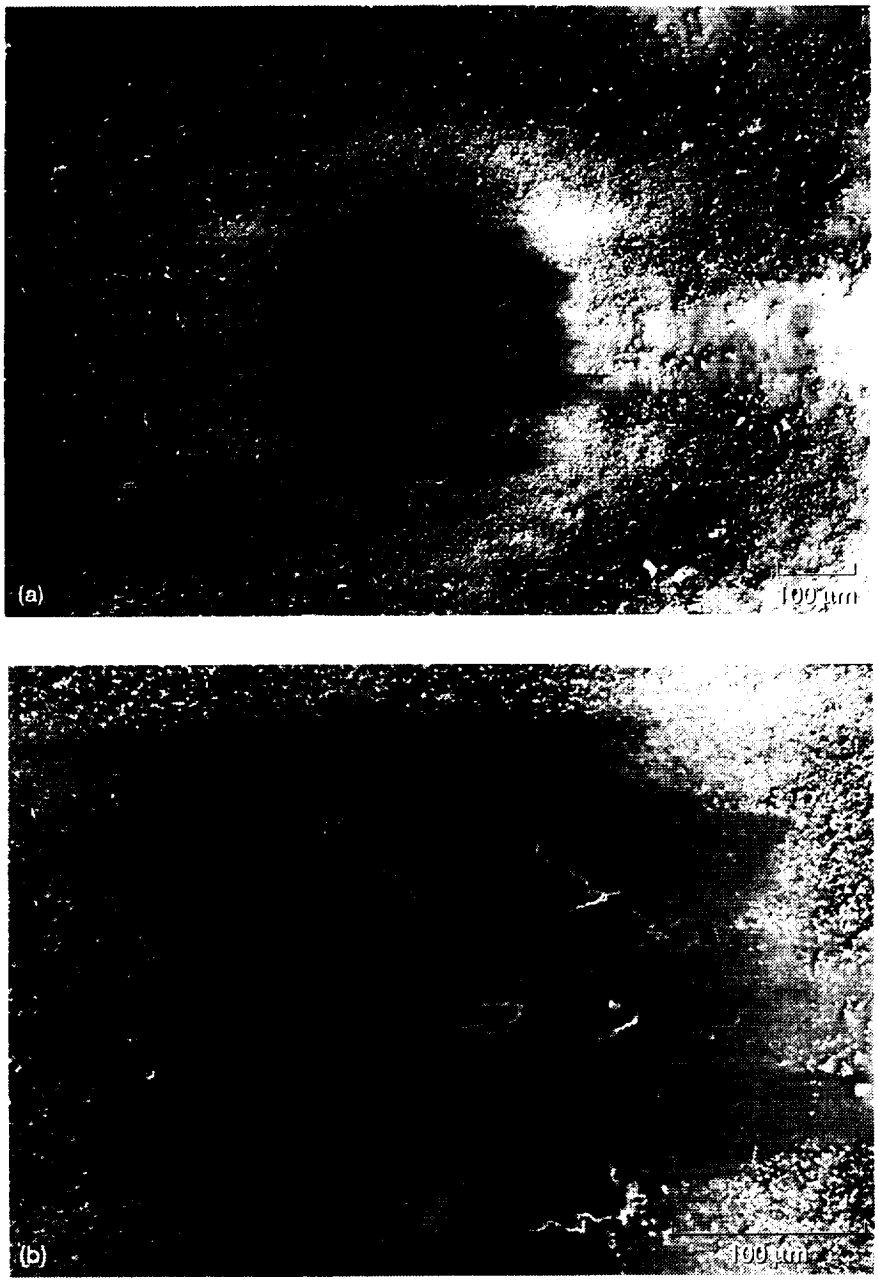

Figure 13.— Wear scar produced on 440C stainless-steel ball after sliding contact with the laser-annealed WS_2 coating at 607 990 passes in ultrahigh vacuum. (a) SEM image at low magnification. (b) SEM image at high magnification.

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13. ABSTRACT (***Maximum 200 words***)

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14. SUBJECT TERMS

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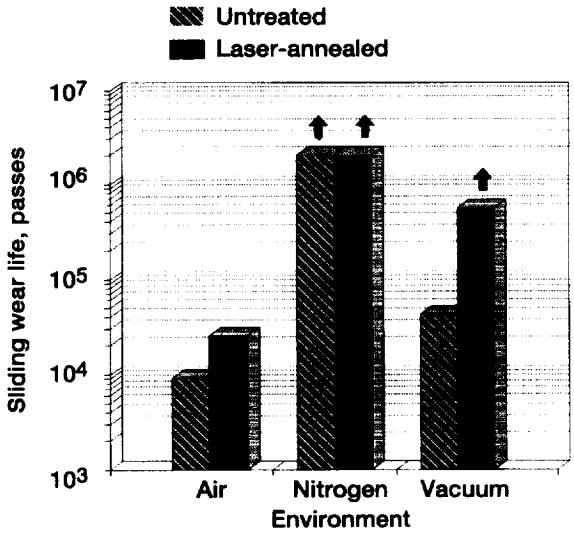

Figure 14.—Sliding wear (endurance) life of untreated and laser-annealed surfaces of pulsed-laser-deposited WS_2 coatings in sliding contact with 440C stainless-steel balls in humid air, dry nitrogen, and ultrahigh vacuum environments.

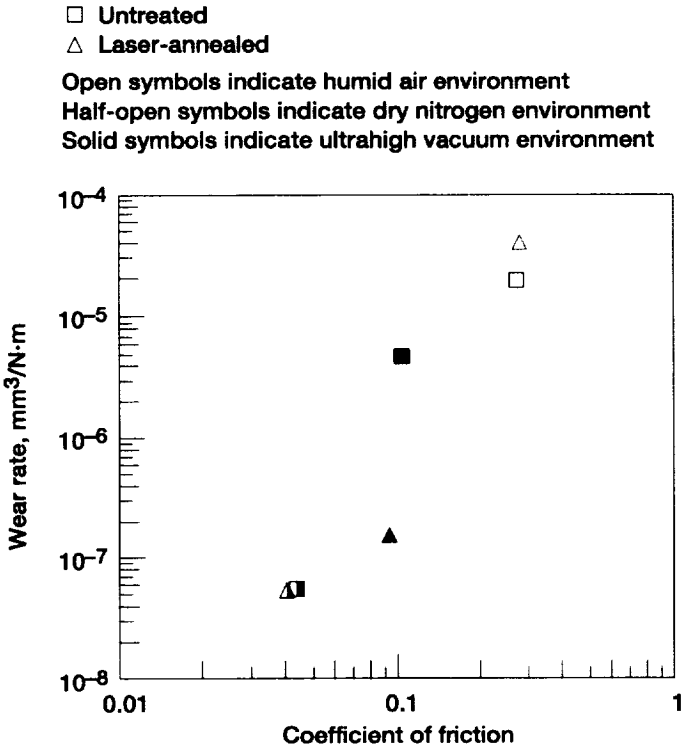

Figure 15.—Steady-state (equilibrium) coefficients of friction and wear rates (dimensional wear coefficient) for untreated and laser-annealed surfaces of pulsed-laser-deposited WS_2 coatings in sliding contact with 440C stainless-steel balls in humid air, dry nitrogen, and ultrahigh vacuum environments.