

Tribology of carbon layers fabricated from SiC exposed to different H₂/Cl₂ gas mixtures

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Silicon carbide-based ceramics are some of the best materials for tribological applications. However, their tribological properties still need to be improved for certain uses under severe conditions. In this study, carbon layers were produced by the exposure of ball and disc type SiCs to various compositions of chlorine-hydrogen gas mixtures at a temperature of 1000 °C for 20 hrs. After the chlorination of the silicon carbide materials, the modified layers were characterized by XRD, Raman, and FE-SEM. The effect of the hydrogen gas content on the carbide-derived carbon (CDC) layers and their resulting tribological properties have been investigated. The tribological behaviors of the CDC layers were studied using a ball-on-disk tribometer. Silicon nitride and chlorinated silicon carbide balls were selected as the counterpart material. The results showed that the wear resistance and frictional coefficients of the surface-modified ball and disk-type SiCs were significantly improved compared to those of untreated silicon carbide specimens. Increasing the hydrogen content of the gas mixture improved the tribological performance of the resulting carbon layers. The use of a higher applied load also improved the tribological performance. The possible mechanisms responsible for the tribological properties of the carbon layers are discussed.

Key words: Silicon Carbide, Chlorination, Hydrogen, Surface roughness, Friction and wear.

Introduction

Ceramic materials, such as silicon carbide, do not have good tribological properties in certain conditions. For example, high frictional coefficients have been reported in unlubricated conditions [1]. So, surface modifications and the addition of reinforcements have been shown to improve their wear resistance at elevated temperatures and in other harsh environments [2, 3].

Recently, carbide-derived carbon (CDC) films fabricated at the surface of ceramic materials have been found to improve their tribological properties. Such materials have shown considerable potential for applications requiring high wear resistance in severe conditions [4, 5]. While several studies have focused on the synthesis and the mechanical and tribological properties of the CDC films, very little is known about the effect of the composition of the H₂/Cl₂ gas mixture on the tribological properties of the resulting CDC film. For example, Gogotsi *et al.* reported that the addition of the hydrogen affected the thickness and structure of the carbon layer [6]. They also reported that the presence of the hydrogen had little effect on the Raman spectrum of the resulting carbon layer, but that it increased its mechanical properties [4]. Systemic investigations of the effect of a hydrogen gas mixture on the tribological properties have been reported previously [6]. In this current study, carbon layers have been fabricated

on the surfaces of SiC samples by exposing them to different H₂/Cl₂ gas mixtures at a fixed temperature of 1000 °C for 20 hrs. The aim of these experiments was to study the effect of the gas mixture composition on the tribological properties of the resulting modified SiC.

Experimental

Fabrication of SiC-derived carbon films

Commercially reaction-bonded SiC disks (each 3 mm thick with a 20 mm diameter) were treated in a tube furnace at 1000 °C and exposed to either 3.5% Cl₂-Ar or various Cl₂-H₂ mixtures. These experiments were performed in order to determine the rates of carbon formation at the surfaces of the samples. A gas mixture containing 5% H₂-95% Ar was blended with a gas mixture of 3.5% Cl₂-Ar such that the ratio of Cl₂ to H₂ in the final mixture ranged from 2 : 0 (only Cl₂) to 2 : 1.9 (up to 48.71% hydrogen). All disks were cleaned in an ultrasonic bath, rinsed in acetone, and placed in an alumina boat before treating in the reaction tube. The specimens were loaded into a fused quartz reaction tube in the furnace, which was purged with the reactive gas mixture before the furnace was heated to 1000 °C. The furnace, containing the specimen within the flowing gas mixture, was held at this temperature for 20 hrs. Each different chlorination reaction was conducted on seven specimens.

Surface and structural characterization

The Raman spectrum of each specimen was recorded by a LabRam HR model (Jobin-Yvon, France) with a LN₂-

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cooled CCD multi-channel detector at room temperature in a conventional backscattering geometry. The spectra were excited with the 514.5 nm line of an Ar-ion laser. In order to be able to measure the carbon layer thicknesses of the treated specimens, the specimens were hot mounted (using a mounting press) in a manner such that cross sections of the carbon layers would be visible after polishing. They were mechanically polished using an 0.5 micrometer diamond spray. For comparison purposes, an untreated SiC reference sample was also examined. The carbon layer thicknesses were determined using a scanning electron microscope (Hitachi S-4300, field emission SEM) that was equipped with a light element energy dispersive spectrometer (Horiba EX-200, EDS). An Alpha-Step (Tencor, P-1) long scan profiler was used to evaluate the surface roughness of each treated specimen. Each roughness data point is the average obtained from ten measurements by an alpha-step surface profiler. Each measurement was obtained from analyzing a $10 \times 10 \text{ mm}^2$ area.

Wear tests

The wear testing was conducted at room temperature using a ball-on-disk type wear tester without any lubricant. Detailed features of this wear tester have been described in a previous study [7]. Untreated and treated SiC balls were slid against a commercially fabricated and polished Si_3N_4 disk. The sliding speed was maintained at about 0.42 m/s in air. The applied loads were selected as 1 N and 5 N. Each test was maintained for 30 minutes. During each sliding loading, the frictional force was measured by a load cell. The signal of the load cell was stored in a computer at a sampling rate of 2 times per second. Then the stored signal was converted to the signal of a frictional coefficient. An average frictional coefficient was calculated from the stabilized signals. Moreover, to quantify the amount of wear experienced by the specimens, the diameters of the wear scars were immediately measured using an optical microscope after testing. Then, the specific wear rate of each specimen was calculated from them.

Each experiment for friction and wear measurements was repeated three times. Note that for each of these measurements, two perpendicular diameters were measured. Thus, each data point was calculated from six diameters in total. After the wear tests, the top and cross-sectional worn surfaces of each sample were examined by SEM.

Results and Discussion

Effect of the H_2/Cl_2 mixture composition on the formation of the carbon layers

Fig. 1 shows typical images of the cross-sections of samples modified by treatment with 27.33% H_2 and 30.46% H_2 . It can be seen that the carbon layer of the specimen treated with 27.33% H_2 was approximately 4 times thicker than that of the specimen treated with 30.46% H_2 . This is also clear in Fig. 2, which shows the variation of the carbon layer thickness as a function

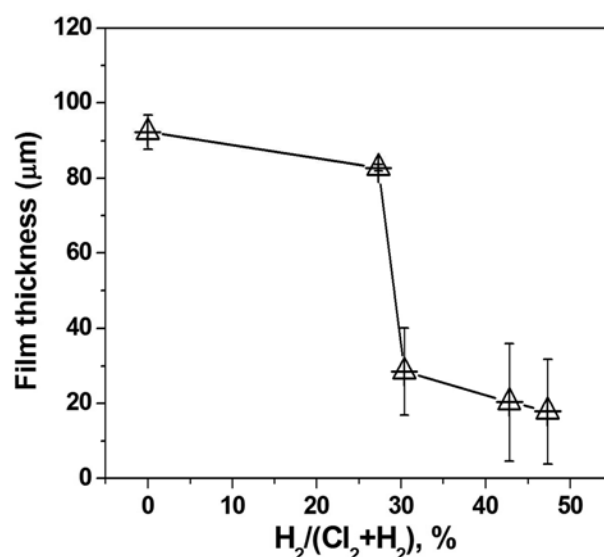
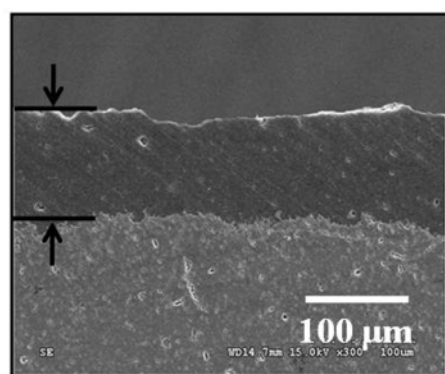
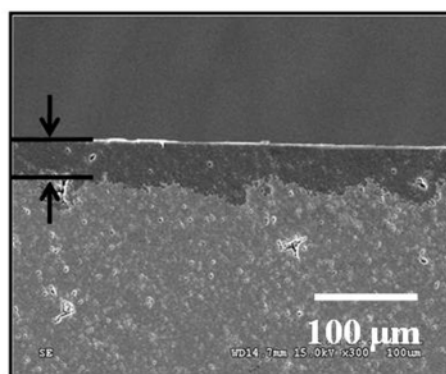


Fig. 2. Dependence of the film thickness on the chlorine/hydrogen ratio of the gas mixture.



(a)



(b)

Fig. 1. SEM micrographs of the cross sections of the samples treated at 1000 °C for 20 hrs with (a) 27.3% H_2 and (b) 30.5% H_2 . The arrows highlight the different layer thicknesses of the carbon formed.

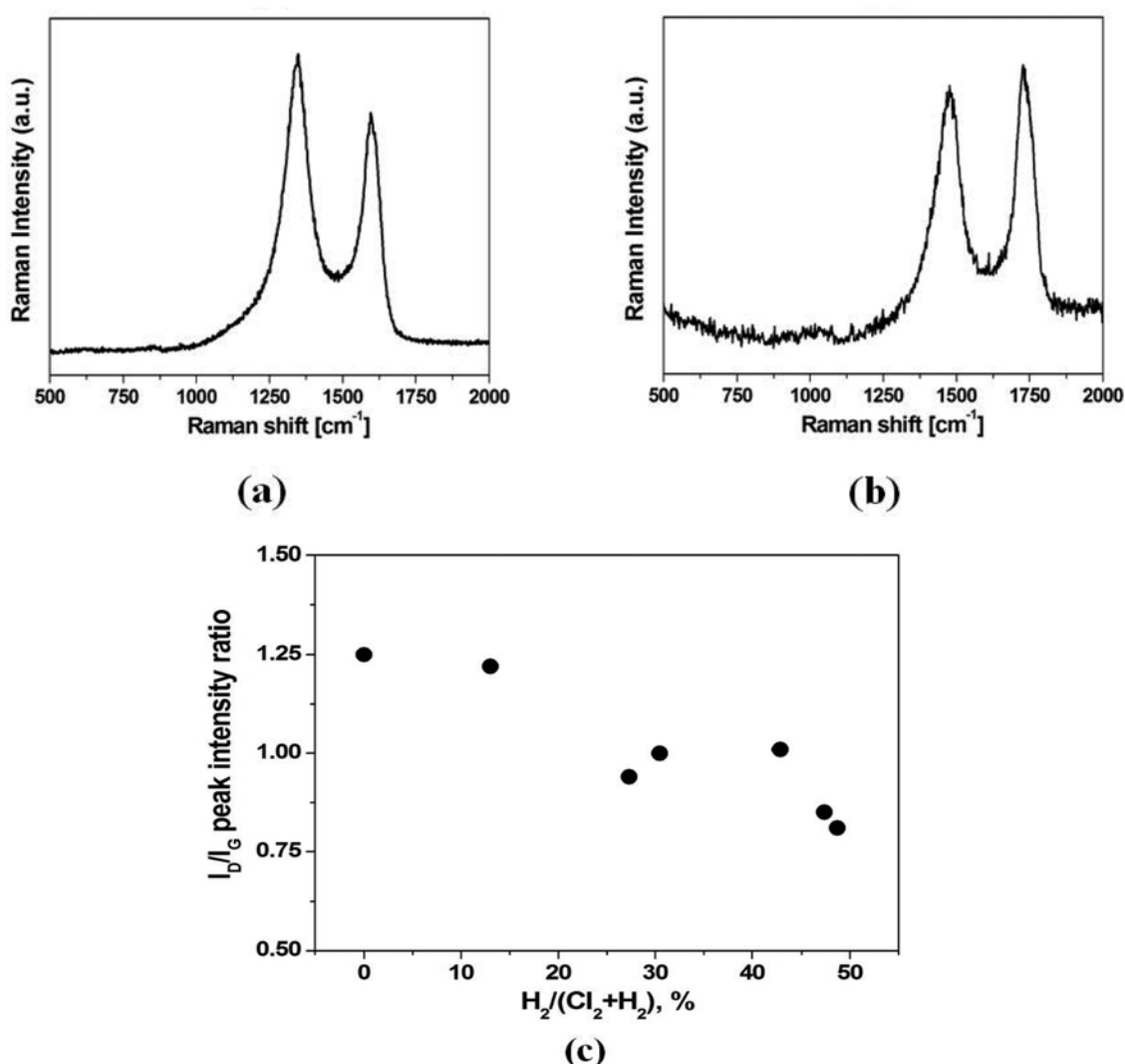


Fig. 3. Raman spectra of the carbon layers synthesized from SiC at 1000 °C for 20 hrs in: (a) only Cl₂ and (b) 48.7% H₂. The effect of the hydrogen content of the gas mixture on the ratio of the intensities of I_D and I_G is shown in (c).

of the hydrogen content of the chlorine-hydrogen mixture. As the hydrogen content in the gas mixture increases, the layer thickness decreases. The sudden drop in layer thickness at about 30% hydrogen might be related to the reducing chlorine potential of the gas mixture by forming the stable HCl, as suggested by Ersoy *et al.* [5].

Fig. 3(a) and (b) show typical Raman spectra of the silicon carbide disks treated in only Cl₂ and 48.7% hydrogen, respectively. Also shown in Fig. 3 is the variation of the I_D/I_G ratio with the different H₂/Cl₂ gas mixtures. The positions and the intensity ratios of the D and G bands depend on the sp³/sp² ratio. The I_D/I_G peak intensity ratio decreased from 1.25 to 0.81 with an increase in the hydrogen content. The I_D/I_G ratio remained at about 1.2 at low hydrogen contents, but decreased significantly at high hydrogen contents. The decrease in the I_D/I_G ratio with increasing H₂ content suggests that a softer carbon layer can form in a higher hydrogen content environment due to the easy formation

of less disordered forms of carbon with its increased cross bonding. These changes in carbon structure might influence the tribological behaviors of the carbon layers.

Tribological properties

Fig. 4 shows the variation of the coefficient of friction with the hydrogen content in the reactive gas mixture. It can be seen that increasing the hydrogen content decreases the coefficient of friction of the material slightly (by up to about 0.1). The frictional coefficients of the original SiC plate under a low and a high load in open air were typically about 0.5 and 0.8, respectively (data not shown). By contrast, the frictional coefficient of a specimen modified through chlorination drops down to below 0.2 due to the formation of the soft carbon layers on the surface. A transition of the frictional coefficient was observed at a hydrogen content of about 30%. Carbon layers formed with higher hydrogen to chlorine ratios exhibited lower frictional coefficients and lower wear rates, as shown in

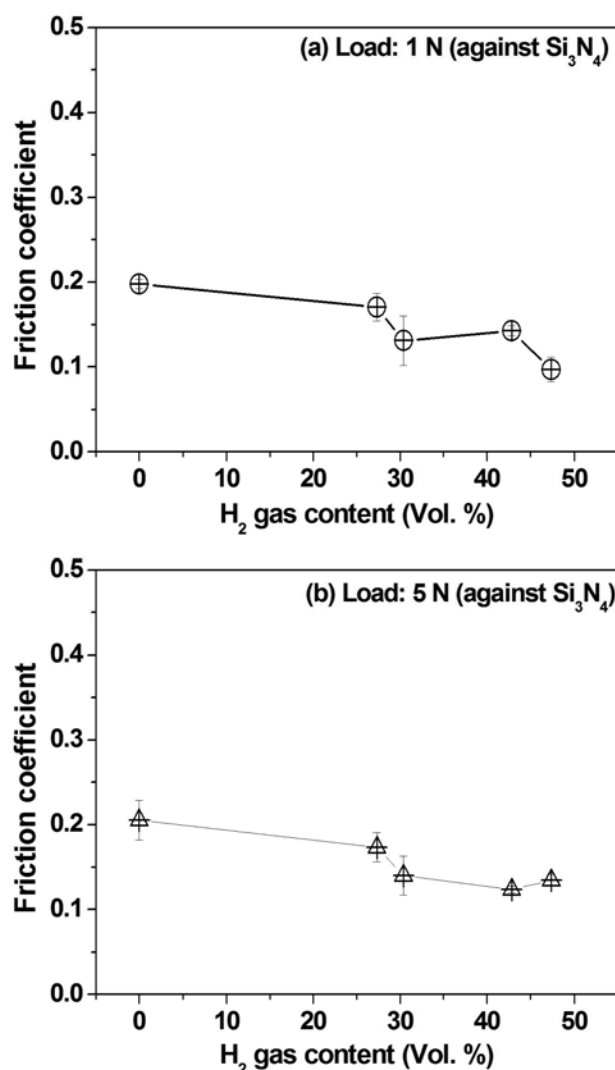


Fig. 4. Variation of frictional coefficients as a function of H_2 gas content under a load of (a) 1 N and (b) 5 N for SiC surfaces modified at 1000 °C for 20 hrs. The tests were carried out by the sliding of Si_3N_4 balls. The frictional coefficients of the original (untreated) SiC are 0.5 and 0.7 at loads of 1 N and 5 N, respectively.

Fig. 4 and 5. We concluded a close correlation between I_D/I_G ratios and tribological behaviors.

The variation of the wear rate upon changing the hydrogen content seems to be similar to the variation of the frictional coefficient, especially for the 1 N load. As shown in Fig. 3, relatively softer carbon layers could have been formed when the hydrogen content was above 30%. Samples treated under such conditions exhibit low friction coefficients and low wear rates due to the easy formation of the soft carbon layers. Our another study by us [8] showed that nanoindentation hardness values decreased from 0.5 GPa to about 0.3 GPa upon increasing the hydrogen content up to 48.5%. The HRTEM results of these specimens in that paper revealed completely transformed carbon films with only several halo rings which suggest amorphous carbon and the hydrogen-etched carbon surface remained with an increase

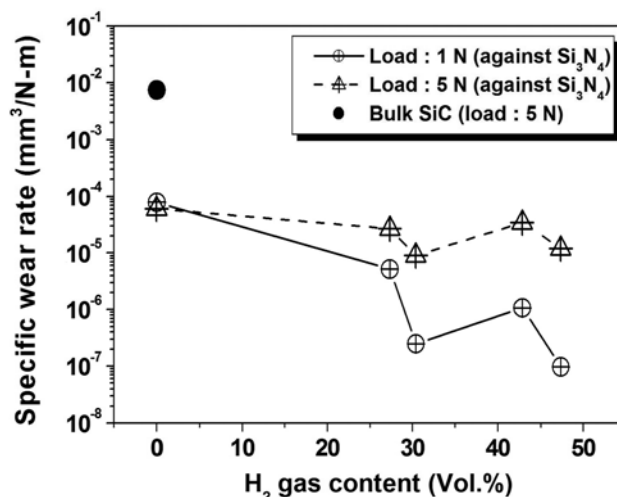


Fig. 5. Specific wear rates of the carbon layers synthesized from SiC at 1000 °C for 20 hrs with the different reaction gas mixtures. Wear tests were carried out using 1 and 5 N loads.

in the hydrogen content at a high chlorination temperature. For the carbon layers fabricated at high hydrogen contents, the higher load (5 N) resulted in higher wear rates than did the lower load (1 N). The difference between wear rates at low and high loads increased with increasing hydrogen content in the gas mixture. This result also indirectly supports the possibility that the effects are due to the increasing soft graphitization of the layers.

Fig. 6 illustrates the average surface roughnesses of the specimens treated with the various compositions of the chlorine-hydrogen mixtures at a temperature of 1000 °C for 20 hrs. It can be seen that increasing the H_2 gas content in the mixture increases the roughness of the resulting carbon layer. The increased roughness

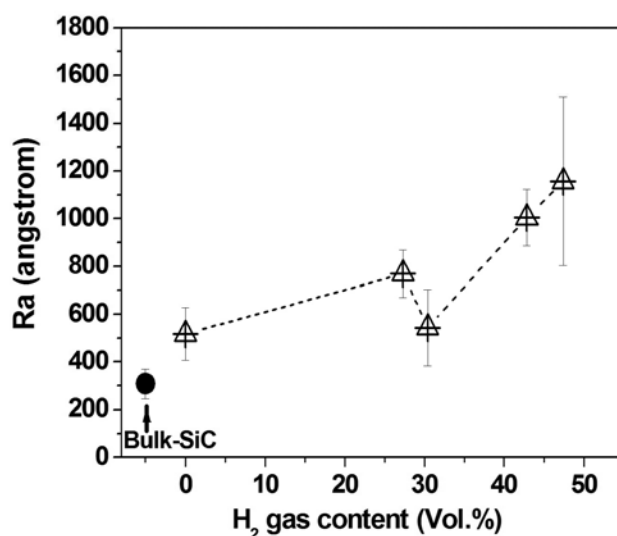


Fig. 6. Influence of the hydrogen content on the surface roughness (Ra) of the SiC disks treated at 1000 °C for 20 hrs in different gas mixtures. The closed circle represents the surface roughness of an untreated SiC disk, as a reference.

might be related to the development of hydrocarbons during the treatment. The increased surface roughness would be expected to increase the layer's frictional coefficient and wear rate. However, the wear performance of the specimen treated with a high hydrogen-content gas mixture has a low friction coefficient and wear rate. This result suggests that surface roughness does not significantly influence the tribological behavior of these carbon layers. This may be because the carbon layers were in the form of graphite, which is soft.

SEM observations of the worn surfaces of the treated SiCs were carried out. Fig. 7 shows that the track observed on the worn surface of a specimen previously treated with only chlorine is wider than those formed on the other specimens. With increasing hydrogen content, the tracks had mainly smooth worn surfaces, as shown

in Fig. 7. After sliding the sample with the thinnest carbon layer (previously treated with the highest hydrogen content) at the high load of 5 N, its surface revealed the brighter underlying SiC substrate (see Fig. 7(e) and (j)). It can also be seen that a small amount of wear debris was produced in the sliding direction.

Conclusions

Treatment of sintered SiC samples with different compositions of H_2/Cl_2 gas mixtures resulted in the formation of carbon layers with different film thicknesses and bonding types. The different bonding types (measured by Raman spectroscopy) directly influenced the frictional coefficients and wear rates of the materials. A correlation between the I_D/I_G ratios to the friction coefficient and specific wear rate was observed. The results suggest that the frictional coefficient and wear rate of the carbon layers can be lowered by controlling the hydrogen content in the reactive H_2/Cl_2 gas mixture.

Acknowledgments

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References

1. I.A. Hutchings, in "Tribology: Friction and wear of engineering materials," (Boca Raton, FL: CRC Press, 1992).
2. H. Hyuga, M. I. Jones, K. Hirao, and Y. Yamauchi, *J. Am. Ceram. Soc.* 87 [4] (2004) 699–702.
3. K. Jia, Y.Q. Li, T.E. Fischer and B. Gallois, *J. Mater. Res.*, 10(6) (1995) 1403–1410.
4. Y. Gogotsi, S. Welz, D.A. Ersoy and M. J. McNallan, *Nature* 411 (2001) 283–286.
5. D.A. Ersoy, M.J. McNallan and Y. Gogotsi, *Mat. Res. Innovat.* 5 (2001) 55–62.
6. Y. Gogotsi, I.-D. Jeon and M.J. McNallan, *J. Mater. Chem.*, 7[9] (1997) 1841–1848.
7. J.-W. An and D.-S. Lim, *J. of Ceramic Processing Research* 3[3] (2002) 118–122.
8. H.-J. Choi, J.-K. Lee, M. J. McNallan and D.-S. Lim, *Diamond and Related Materials*, (2008) in preparation.

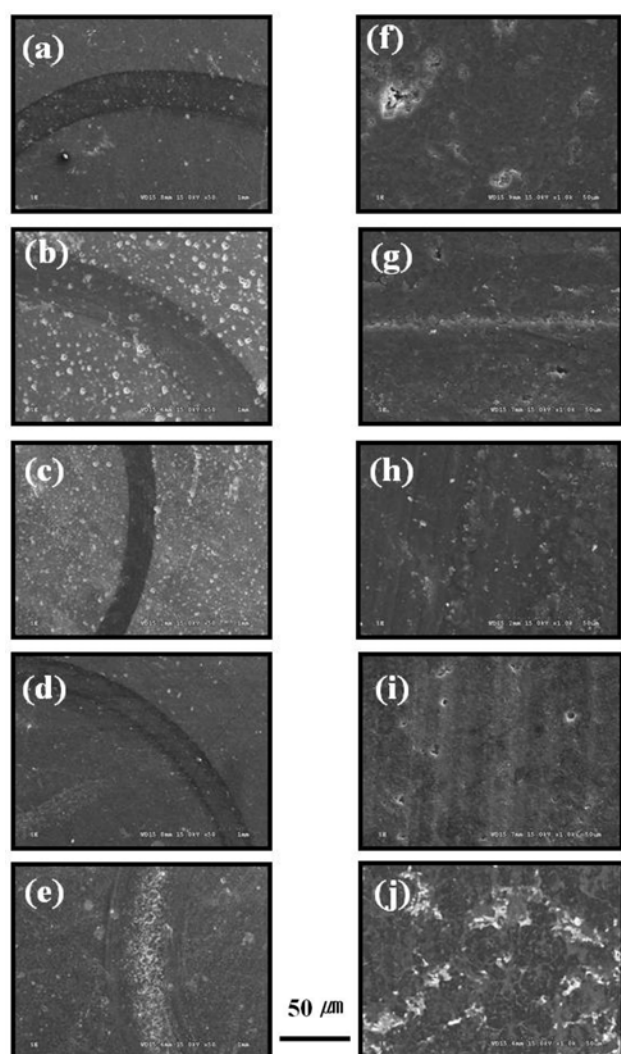


Fig. 7. Microstructures of the worn surfaces of the specimens previously chlorinated with the gas mixtures containing the following: (a) only Cl_2 , (b) 27.3% hydrogen, (c) 30.5% hydrogen, (d) 42.9% hydrogen, and (e) 47.4% hydrogen. The centers of the wear tracks in (a) to (e) are shown at a higher magnification in (f) to (j), respectively. The test sample was slid against a Si_3N_4 ball using a load of 5 N.