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Macroscopic Wear Behavior of C/C and C/C-SiC Composites Coated with Hafnium Carbide

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ABSTRACT

This study investigates the macroscopic wear behaviors of C/C and C/C-SiC composites coated with hafnium carbide (HfC). To improve the wear resistance of C/C composites, low-pressure chemical vapor deposition (LPCVD) was used to obtain HfC coating. The CVD coatings were deposited at various deposition temperatures of 1300, 1400, and 1500°C. The effect of the substrate material (the C/C substrate, the C/C-CVR substrate, or the C/C-SiC substrate deposited by LSI) was also studied to improve the wear resistance. The experiment used the ball-on-disk method, with a tungsten carbide (WC) ball utilized as an indenter to evaluate the wear behavior. The HfC coatings were found to effectively improve the wear resistance of C/C and C/C-SiC composites, compared with the case of a non-coated C/C composite. The former showed lower friction coefficients and almost no wear loss during the wear test because of the presence of hard coatings. The wear scar width was relatively narrower for the C/C and C/C-SiC composites with hafnium coatings. Wear behavior was found to critically depend on the deposition temperature and the material. Thus, the HfC-coated C/C-SiC composites fabricated at deposition temperatures of 1500°C showed the best wear resistance, a lower friction coefficient, and almost no loss during the wear test.

Key words : Wear, C/C composite, Hafnium carbide, Coatings

1. Introduction

Carbon-carbon- (C/C) or carbon-fiber-reinforced silicon carbide (C/C-SiC) composites are thermally and mechanically superior materials used in aeronautical, environmental, and structural applications.[1-7] C/C composites have seen application as nose caps, leading edges, and thermal protection systems of supersonic aircraft, as well as in exhaust cones, casting struts, secondary nozzle flaps, and primary nozzle flaps of gas turbine systems.[7] The C/C composite has the primary advantage of being more lightweight than alloys or other engineering ceramics. C/C composites are fabricated by weaving fibers and filling fiber voids with matrix material to improve the composite's mechanical properties. The chemical vapor reaction (CVR) and liquid silicon infiltration (LSI) methods are used to fill the voids with matrix material, so as to increase the density of the matrix in the final composite structure.[8-10] Nevertheless, one of the disadvantages of the C/C composites are their inferior oxidation resistance, as carbon is easily oxidized in high-temperature oxidizing environments. The oxide layer deposited on the surface of the composite can also be converted to volatile species in the presence of water vapor at high temperatures. The unmatched oxide or corroded layer can form small cracks, leading to defoliation and causing severe degradation of the composites.[11-14)]

To overcome the problems of ablation and reactions with oxygen and water vapor, protective coatings have been widely studied. Among them, hafnium (HfC) coating, due to its high melting point and lower evaporation rate, has been found to be a promising material for protecting C/C composites. HfC coating was found to effectively protect C/C composites during a serious flame test. A reactive infiltration technique was used in the study.[15] The SiC/HfC/SiC coatings were found to improve the ablation resistance of the C/C composite.[16] The researchers introduced multiple layers to reduce the thermal expansion mismatch between the HfC and the C/C composites. HfC/ZrC protective coating was also studied by means of low-pressure chemical vapor deposition (LPCVD) in an $HfCl_4$-$ZrCl_4$-CH_4-H_2-Ar system. The composite coating was found to decrease ablation rates.[17]

In this study, HfC coating was applied to a carbon-based composite by LPCVD. Protection performance was evaluated using the ball-on-disk method, using a tungsten carbide (WC) ball. The deposition temperature was controlled as the HfC layer was deposited; we also studied the effect of different substrate materials (the C/C composite, the C/C-CVR substrate, and the C/C-SiC substrate deposited by LSI). The results show the wear behavior to be dependent on the deposition temperature and the material; the HfC coating was found to be very effective for protection.

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2. Experimental Procedure

For wear evaluations, the C/C composite samples (each with a diameter of 30 mm) were punched using needles from an OXI-PAN fiber web to yield a reinforced preform, which was then carbonized at 1700°C. The preform was then impregnated with coal-tar pitch and carbonized at 2200°C via heat treatment. The impregnation–heat treatment process was performed several times to yield a C/C preform with a specific density of 1.78 g/cm^3.

The C/C-CVR substrates, reacted by chemical vapor reaction (CVR), were prepared in an Si gasification furnace. The gasified Si reacted with the carbon matrix on the surface of the C/C composite and changed into an SiC layer, with a depth of 100 - 200 μm on the surface of the composite. The density of the C/C substrates deposited by CVR increased to 1.84 g/cm^3.

In this study, the C/C-SiC samples were produced using a liquid silicon infiltration (LSI) process. The C/C composites were in contact with Si powder (Elkem, 0.8 mm, Norway) in a graphite crucible. The crucible was placed in a graphite resistance furnace, slowly heated to 600°C to remove the organic additive, and heated to 1650°C in a vacuum of 13.3 Pa (10^{-1} torr) for 30 min. Finally, the melted metal silicon reacted with the carbon matrix in the C/C preform to form SiC. Therefore, the density of the C/C substrate deposited by LSI increased to 2.14 g/cm^3 because of the SiC.

HfC coating was deposited on each sample material (the C/C substrate, the C/C-CVR substrate, or the C/C-SiC substrate deposited by LSI), using a conventional two-zone horizontal tube furnace in the temperature range of 1300–1500°C for 3 h under atmospheric pressure conditions. The deposition of HfC arose from the reaction of $HfCl_4$, C_2H_4, H_2, and Ar, in which $HfCl_4$ (Sigma Aldrich Co., USA, sublimation temperature = 590°K) was used as a hafnium precursor, C_2H_4 as a carbon source, H_2 as a reducing gas, and Ar as a carrier gas. The precursor of hafnium, $HfCl_4$, was heated so that it would sublimate and taken into the chamber by a carrier gas. The gas flow rates of C_2H_4, H_2, and Ar were controlled at 40, 400, and 400 ml/min, respectively. The coating thickness was controlled at ~10 μm.

The wear test was evaluated by the ball-on-disk method. The samples were slightly ground with diamond paste to level off their surfaces. WC spheres with r = 1.98 mm or 3.18 mm were used, and a fixed load of P = 29.4 N was applied to the sample. The contacted ball, fixed under a constant load, rotated on the disk sample along the trace of a circle with a diameter of 20 mm. The rotating speed remained at a constant value of 60 rpm. A friction load sensor was used to measure the friction coefficient, and the number of cycles was found to be 300. The wear loss was calculated based on the weight change during the test. The resulting wear scars were observed via video microscope.

3. Results and Discussion

3.1. Effect of deposition temperature and coating

Figure 1 shows the friction coefficients of the C/C composite without coating and the HfC deposited on the C/C composite, at temperatures of 1300°C, 1400°C, and 1500°C. Each coefficient was plotted as a function of the number of cycles in the wear test, which used a WC ball with r = 3.18 mm under a load of P = 29.4 N and a velocity of 60 rpm for 300 cycles. The friction coefficients of the C/C composite without coating were found to change as the number of cycles increased. On the other hand, the HfC deposited on the C/C composite yielded relatively constant friction coefficients. These results indicate that the wear behavior of the C/C composite can be improved with an HfC coating. In particular, the friction coefficients of the HfC coated on the C/C composite (fabricated at higher temperatures of 1400°C and 1500°C) were much lower than those whose coatings were deposited at 1300°C.

Figure 2 shows the weight loss of the C/C composites with-

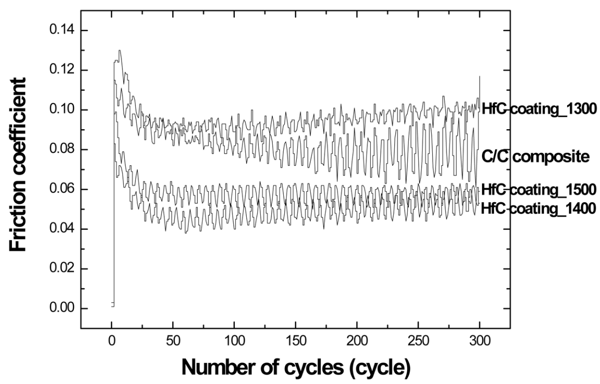

Fig. 1. Friction coefficient of C/C composites as a function of the number of cycles in the wear test using a WC ball with r = 3.18 mm. The friction coefficients of the C/C composite (No coating) and HfC deposited on the C/C composite at different temperatures of 1300, 1400, and 1500°C are plotted in the graph.

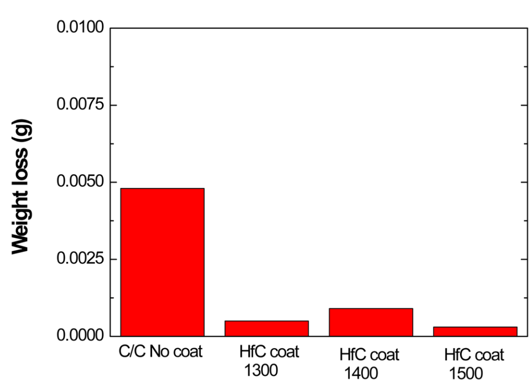

Fig. 2. Weight loss of C/C composites in the wear test using a WC ball with r = 3.18 mm. The wear losses of the C/C composite (No coating) and HfC deposited on the C/C composite at different temperatures of 1300, 1400, and 1500°C are represented in the graph.

out coating and of the HfC deposited at different deposition temperatures of 1300°C, 1400°C, and 1500°C. While weight changes occurred for the C/C composites without coating, there were almost no changes in weight for the HfC-coated composites at the given wear test conditions.

Figure 3 plots the friction coefficients of the C/C composite without coating and of the HfC deposited on the C/C-CVR substrate. The HfC coating was deposited on the C/C-CVR substrate at different deposition temperatures of 1300 and 1500°C. The wear test was conducted at load P = 29.4 N with a speed of 60 rpm for 300 cycles, using a ball with r = 1.98 mm, which is a smaller-sized ball than those used in Figs. 1 and 2. While the C/C composite without coating showed significant changes after 50 cycles in the friction coefficient curve, the HfC coated on the C/C-CVR substrate showed almost no changes, except in the range of 200 to 300 cycles for the HfC coated sample fabricated at 1300°C. The HfC deposited on the C/C-CVR substrate fabricated at 1500°C maintained the smallest friction coefficient during the wear test, indicating relatively higher wear resistance.

When we compare the friction coefficients shown in Fig. 1 and Fig. 3, we note that when a ball with r = 1.98 mm was used, more significant changes occurred in the friction coefficients of the C/C composites without coating. This result emerged because the decreased area had higher contact stress for a smaller contact ball.[18] It is noteworthy that the HfC deposited on the C/C composite or the C/C-CVR deposited at 1500°C maintained a constant friction coefficient, even though the experimental parameters of both the substrate material and ball size had changed. As can be seen in Fig. 4, relatively less wear loss was observed with the HfC coating, and much less wear loss was observed for HfC deposition at a higher deposition temperature of 1500°C. We observed significant wear loss on the surface of the C/C composite without coating due to contact with the WC ball, but the loss diminished dramatically with HfC coating. These results are related to the wear rate, which depends on the hardness of the disk sample. The literature shows that the hardness of HfC is higher than that of C and SiC ceramics.[15)]

Figure 5 records the widths of the wear scars, measured by video microscope, that were produced on the surface of

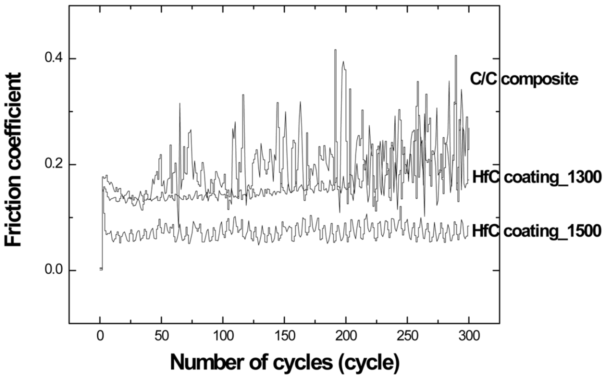

Fig. 3. Friction coefficients of C/C composites or HfC-coated C/C composites reacted by CVR as a function of the number of cycles in the wear test using a WC ball with r = 1.98 mm. The friction coefficients of the C/C composite (No coating) and HfC deposited on the C/C-CVR composite at different temperatures of 1300 and 1500°C are plotted in the graph.

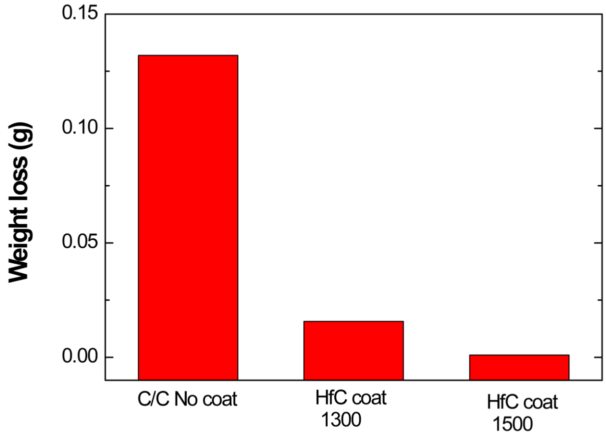

Fig. 4. Weight loss of C/C composites or HfC-coated C/C-CVR composites in the wear test using a WC ball with r = 1.98 mm. The wear losses of the C/C composite (No coating) and of HfC deposited on the C/C-CVR substrate, fabricated at different temperatures of 1300 and 1500°C, respectively, are represented in the graph.

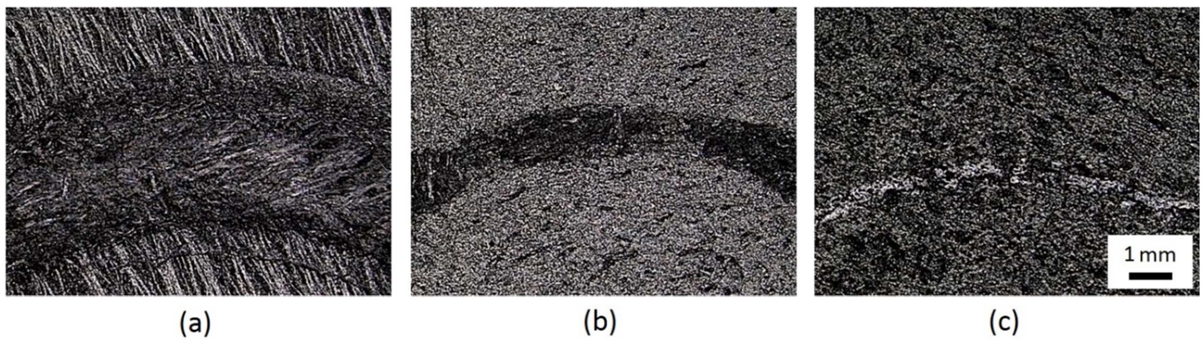

Fig. 5. Video microscope images of wear scars obtained using a WC ball with r = 1.98 mm, produced on the surface of (a) Non-coated sample on the C/C-CVR substrate, (b) HfC coating on the C/C-CVR substrate, deposited at 1300°C, and (c) HfC coating on the C/C-CVR substrate, fabricated at 1500°C.

the C/C composite without coating and on the HfC deposited on the C/C-CVR substrate, at different temperatures of 1300 and 1500°C, respectively. The test was conducted at a load of P = 29.4 N and a speed of 60 rpm, using a WC ball with r = 1.98 mm for 300 cycles. It is clear that the size of the wear scars diminished, indicating that the presence of HfC coating led to high wear resistance of the C/C composite. The pictures show primarily abrasive wear; strong fibers remained in the damaged region, indicating that fiber pull-out occurred.

Therefore, it is clear that HfC coating reduced the friction coefficient, wear loss, and width of the wear scars. The wear resistance was most improved for the sample of HfC deposited at the higher temperature of 1500°C. The effect of the deposition temperature has been studied in the literature.[19] Delamination of the coating did not occur during the test.

3.2. Effect of substrate material

Figure 6 shows the friction coefficient of HfC deposited on different substrate materials: the C/C composite substrate, the C/C-CVR substrate, and the C/C-SiC substrate fabricated at 1300°C. The coefficient was plotted as a function of the number of cycles in the wear test, which used a WC ball with r = 1.98 mm at a load of P = 29.4 N and a velocity of 60 rpm for 300 cycles. The results indicate that the friction coefficient changes depend on the substrate material. Significant wear occurred on the HfC sample deposited on the C/C composite substrate. However, the friction coefficient was reduced when the substrate was changed to the C/C-CVR substrate. Moreover, the friction coefficient of the C/C-SiC composite, reacted by LSI, showed no change in the given range of number of cycles.

The changes in friction coefficient were influenced by the changes in weight, as shown in Fig. 7. While the C/C composite without coating showed the largest weight change, the other changes varied depending on the substrate material. As a result, we found that the wear loss was reduced when the substrate material was changed to the C/C composite with HfC coating, HfC deposited on the C/C-CVR substrate, and the C/C-SiC substrate reacted by LSI. Notably, there was almost no weight change for the HfC deposited on the C/C-SiC composite, reacted by LSI.

Figure 8 shows the widths of the wear scars that were observed on the surfaces of the HfC coatings with different substrates. The width of wear scars was smallest for the HfC deposited on the C/C-SiC substrate reacted by LSI, which was tested using a WC ball with r = 1.98 mm at a load of P = 29.4 N and with a velocity of 60 rpm. This result agrees closely with the constant friction coefficient observed in Fig. 6 and shows almost no weight change from that observed in Fig. 7.

The effect of substrate material has been studied in the literature. When a wear experiment is conducted under constrained conditions, the use of a material with a different elastic modulus has an effect on the damage and wear

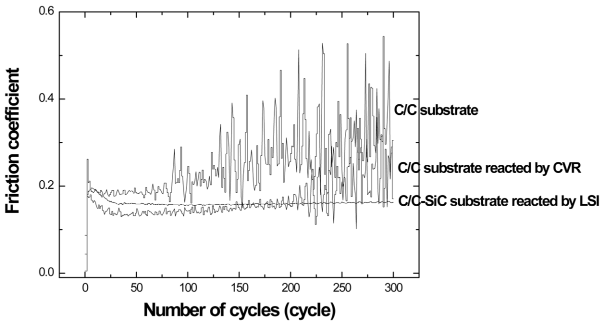

Fig. 6. Friction coefficients of HfC coatings deposited on the different substrates: C/C substrate, C/C-CVR substrate, or C/C-SiC substrate reacted by LSI. The coefficients are plotted as a function of the number of cycles in the wear test using a WC ball with r = 1.98 mm.

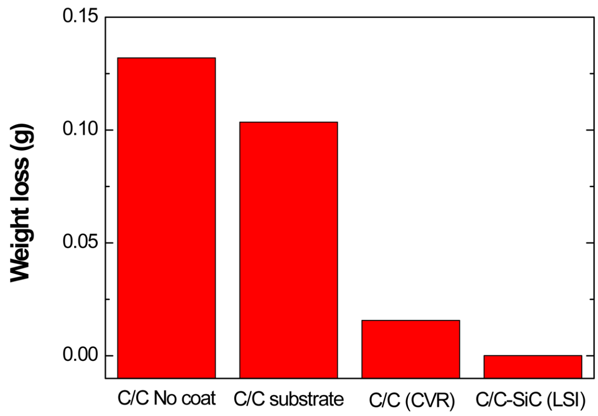

Fig. 7. Weight loss of HfC coatings deposited on the different substrates: C/C substrate, C/C-CVR substrate, or C/C-SiC substrate reacted by LSI. The wear test was conducted using a WC ball with r = 1.98 mm. The wear loss data of C/C composites without coating are inserted.

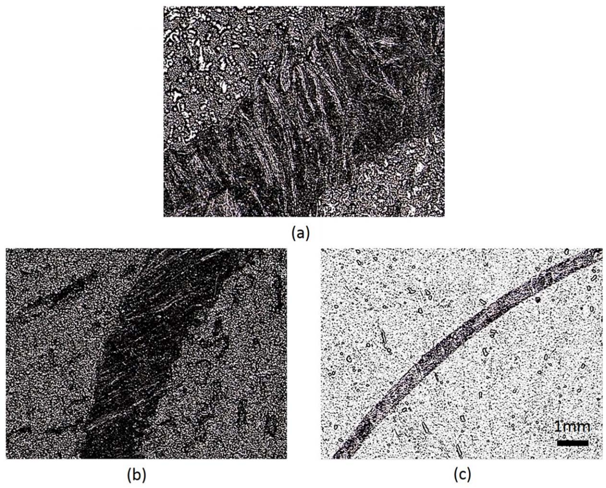

Fig. 8. Video microscope images of wear scars of HfC coatings deposited on the different substrates: (a) C/C substrate, (b) C/C-CVR substrate, and (c) C/C-SiC substrate reacted by LSI. The wear test was conducted using a WC ball with r = 1.98 mm.

behavior.[20,21] A hard substrate is desirable for resisting the flexural stress found in the hard/soft coating/substrate material system.[22] Residual stress is another significant factor influencing wear behavior.[23] Because the thermal expansion coefficient of HfC is larger (6.6×10^{-6}/°C, compared to the carbon composite's coefficient of 1 - 2×10^{-6}/°C or silicon carbide's coefficient of 3 - 4×10^{-6}/°C),[16] the residual tension stress will remain on the coatings during cooling. A higher-density substrate may influence the thermal expansion coefficient.[24] The effect of coating thickness was found to be negligible in this study, because the coating experimental conditions are the same for all substrates. Detailed microstructural studies are forthcoming in our future research.

4. Conclusions

WC ball-on-disk characterization was used to investigate the macroscopic wear behavior such as the friction coefficient, wear loss, and wear scar width of HfC deposited on the C/C composite, the C/C-CVR composite, or the C/C-SiC composite. The wear behaviors were then compared with that of a C/C composite without HfC coating.

The use of a harder HfC coating reduced the friction coefficient and wear loss of C/C, C/C-CVR, and the C/C-SiC composites. As a result, it can be confirmed that when HfC coating is present, the wear resistance of the composite is improved.

The wear behaviors of HfC deposited on different substrates, including the C/C composite, the C/C-CVR composite, and the C/C-SiC composite reacted by LSI, were also investigated. The choice of substrate was found to have a critical impact, and the use of a higher-density C/C-SiC substrate effectively improved the wear resistance in the HfC-coated system.

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