JMEPEG (2004) 13:439-444
DOI: 10.1361/10599490419928

1059-9495/$19.00

Composite Coatings Incorporating Solid Lubricant Phases

J.E. Krzanowski, J.L. Endrino, J.J. Nainaparampil, and J.S. Zabinski

(Submitted February 10, 2004)

The concept of incorporating a solid lubricant, silver (Ag), within a hard carbide film for vacuum tribology applications is investigated in this paper. SiC/Ag and HfC/Ag films were deposited by magnetron cosputtering at 200 °C onto Si and 440C steel substrates. The composition, phase structure, and morphology in these films was examined using x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy. The microstructural analysis showed that Ag was incorporated both within and on the surface of the films. There was a strong tendency for Ag to segregate to the film surface. Vacuum tribology tests were conducted using a ball-on-disk test in a vacuum of 1.33 μPa with a 1 N load for 10 000 cycles. For both the SiC/Ag and HfC/Ag films, the average friction coefficients were reduced when sufficient Ag was present. These tests show that carbide-Ag composite films hold promise for vacuum tribology applications.

Keywords carbides, friction, hard coatings, solid lubricants, tribology

1. Introduction

Soft, lubricious coatings are needed to make precision parts resistant to adhesive wear and surface fatigue. New tribological coatings that can reduce the wear of mechanical components and decrease the use of liquid lubricants are needed for operation in vacuum environments. Soft coatings commonly used in vacuum environments include dichalcogenides such as molybdenum disulfide and tungsten disulfide, and soft metals such as silver (Ag) or gold (Au). However, the applicability of soft coatings can be limited by their high wear rate at high loads. One solution to this problem is to combine hard and lubricant layers in a film to adequately support the lubricant and decrease the wear rate.

An additional advantage of a nanocomposite hard/lubricous coating is that it may be suitable for operation in multiple environments. For example, Voevodin et al.[1,2] investigated nanocomposite coatings that achieve surface self-adaptation through chemical and structural changes due to different loads and environments. One of the most successful coatings was WC/DLC/WS_2, which exhibited a low friction coefficient in a vacuum environment (~0.03) and excellent friction recovery between dry and moist air environments.[3] The low friction exhibited under vacuum was attributed to the weak Van der Waals forces between the hexagonal basal planes of WS_2, while the low friction in air was related to the formation of a graphite-like transfer film. The coatings were labeled as "chameleons" due to the ability of the coating to adapt to different environments. More recently, an attempt was made to extend the chameleon effect to include high-temperature environments. YSZ/Au/MoS_2/diamondlike (DLC) coatings were designed for this purpose.[4] Similar to WC/DLC/WS_2, friction results for YSZ/Au/MoS_2/DLC indicated excellent endurance in vacuum, dry nitrogen, and humid air, but low endurance at high temperatures.

The applicability of lubricant nanocomposite coatings can also be extended to biomedical applications. For instance, recently, Narayan et al.[5] demonstrated the advantages of incorporating nanocrystalline Ag particles into a DLC film for use in biomedical implanted devices. The antimicrobial effect of Ag reservoirs helps reduce the infections associated with biomedical implants and at the same time helps decrease the internal stress of the DLC films, which usually leads to poor adhesion and peel off. These results underscore the beneficial effects of solid lubricant reservoirs in a hard amorphous matrix.

In recent research, the vacuum tribological properties of composite coatings consisting of carbides and Ag have been investigated. Previous investigations have been conducted on WC/Ag and TiC/Ag[7] deposited by magnetron sputter deposition and TiC/Ag deposited by a combined pulsed laser-deposition and magnetron sputtering method.[8] In these studies, it was found that the metal carbide and Ag components form separate phases. However, the microstructure of the film, particularly, whether the Ag phase forms within or on the surface of the film, is dependent on the particular carbide used as well as the Ag concentration. Nevertheless, with a sufficient Ag content (~15-25% Ag), the friction coefficient was reduced in vacuum when tested against a 440C steel ball counterface, in comparison to the carbide alone.

In the present paper, previous investigations on films of SiC/Ag and HfC/Ag are reviewed and extended.[9] Films were deposited by radio frequency (rf) magnetron cosputtering of the carbide and Ag components and were tested in vacuum environments to determine the effects of Ag content on friction

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This paper was presented at the 2nd International Surface Engineering Congress sponsored by ASM International, on September 15-17, 2003, in Indianapolis, Indiana, and appears on pp. 554-59 of the Proceedings.

J.E. Krzanowski and **J.L. Endrino,** Mechanical Engineering Department, University of New Hampshire, Durham, NH; and **J.J. Nainaparampil** and **J.S. Zabinski,** Air Force Research Laboratory, MLBT, Wright-Patterson AFB, OH. Contact e-mail: jamesk@cisunix.unh.edu.

coefficients. New results presented here on x-ray photoelectron spectroscopy (XPS) depth profiles demonstrate the strong tendency for Ag to segregate to the film surface.

2. Experimental Methods

Films for this study were deposited in a dual rf magnetron sputtering system. The system consisted of a high-vacuum deposition chamber with a base pressure of 6.7×10^{-5} Pa that was back-filled with high-purity argon to a pressure of 1.33 Pa during sputtering. The two sputter guns were powered by two rf power supplies. Films were deposited on both Si wafers and 440C stainless steel substrates at 200 °C. Typical film thickness was 1 μm.

The bulk composition of the deposited films was determined by energy-dispersive x-ray spectroscopy in a scanning electron microscope (SEM; Amray 3300FE SEM). Because this is not a reliable method for quantitatively determining carbon concentrations, film concentrations are reported as a percentage of Ag relative to the total Ag + Hf or Ag + Si content. As is shown in the following section, the distribution of Ag in these films is nonuniform (with respect to depth). The bulk compositions reported are, therefore, dependent on the depth of electron penetration versus the film thickness, so the values reported can only be regarded as an estimate of the actual bulk composition. XPS was used to investigate the Ag concentration as a function of depth. XPS experiments were carried out on a Kratos Analytical Axis/HS (Chestnut Ridge, NY) instrument using a Mg K_α x-ray source. The elemental composition determined after ion etching in the XPS with Ar^+ ions for given periods of time.

The microstructure of the films in cross section was determined using two methods: First, films deposited on Si could be examined in the SEM by looking at a fracture edge. Second, samples were polished using standard metallographic techniques. However, due to the limited film thickness, the samples were oriented with the substrate surface at a small angle to the polished section surface, effectively creating a taper section. After polishing, these samples were ion-etched using 3.5 kV Ar^+ ions to help reveal the microstructure. These samples were also examined in the SEM.

To determine the phases present, x-ray diffraction (XRD) was carried out on thin films deposited on the silicon wafers. A Rigaku DMAX/B (Rigakul/MSC, The Woodlands, TX) instrument was used and operated with a Cu K_α x-ray tube. The vacuum tribology experiments were carried out on a high vacuum ball-on-flat tribometer. A 6.25 mm diameter 440C steel ball was used as the counterface. The typical pressure in the chamber was 1.33×10^{-6} Pa. The rotational speed depended on the track radius and was adjusted to get a constant sliding speed of 50 mm/s. The friction measurements were made at a normal load of 1 N. For steel-on-steel, a normal load of 1 N on a 6.25 mm diameter ball corresponds to a maximum Hertzian contact pressure of 425 MPa.

3. Results

3.1 SiC/Ag Films

The deposition parameters and film compositions are listed in Table 1 for the SiC/Ag films. The compositions range from 0-50.8 at.% Ag. XRD analysis of these films revealed that the SiC was present mostly in the amorphous state. Figure 2 shows an XRD pattern for sample SiCAg-6, containing 50.8% Ag. The Ag peaks are clearly present, indicating that Ag is present in the metallic, crystalline state. An additional broad peak is present that is most likely due to the amorphous SiC.

Several films were examined in the SEM to determine their microstructure and surface morphology. SEM images of the surface of the deposited films (before tribological testing) are shown in Fig. 2 for films with 2.1%, 36%, and 50.8% Ag. The surfaces of the films with 2.1% and 36% Ag show an increasing density of lighter-colored nodules on the surface. Due to the high secondary electron emissivity of Ag in comparison to SiC, the nodules are likely to be Ag; however, because they are submicron in size, analysis with energy-dispersive x-ray (EDX) was not possible. For the film with 50.8% Ag, the Ag appears to completely coat the surface. Figure 3 shows a SEM image of a fractured edge of the film with 36% Ag. This image again shows a lighter colored surface layer, which is consistent with the surface image. Within the film, the microstructure appears to vary with depth. The lower portion of the film (near the substrate) contains lighter-colored particles that are typically less than 0.1 μm in diameter, which were tentatively identified as Ag. However, closer to the film surface, these Ag particles are not present. This indicates that the Ag close to the film surface has diffused to the surface, while Ag closer to the substrate remains embedded in the film as distinct particles.

Table 1 Sputter Deposition Parameters and Ag Concentrations of SiC/Ag Films

Sample	SiC Gun Power, W	Ag Gun Power, W	Ag (a), at.%
SiCAg-1	200	0	0
SiCAg-2	200	5	2.1
SiCAg-3	200	10	7.4
SiCAg-4	200	15	21.7
SiCAg-5	200	20	36
SiCAg-6	200	25	50.8

(a) Ag content is relative to Ag + Si total

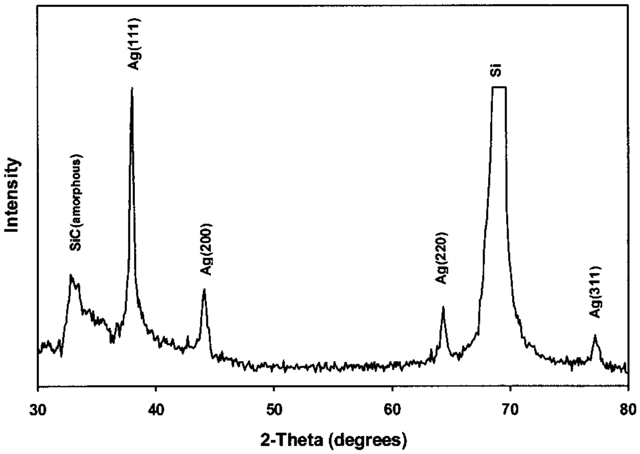

Fig. 1 XRD spectrum for sample SiCAg-6, showing peaks for crystalline Ag and amorphous SiC

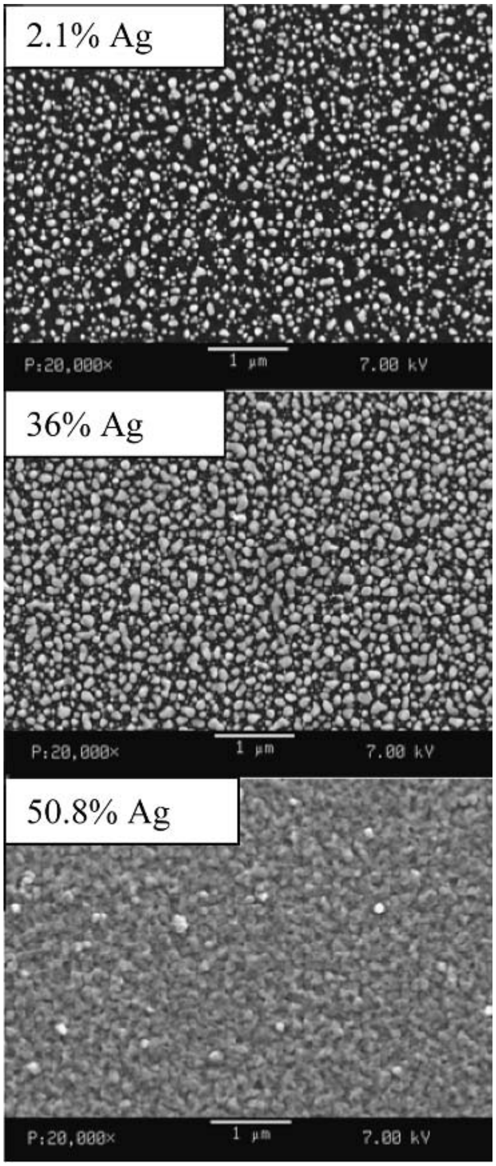

Fig. 2 SEM images of SiC/Ag film surface for films with increasing amounts of Ag

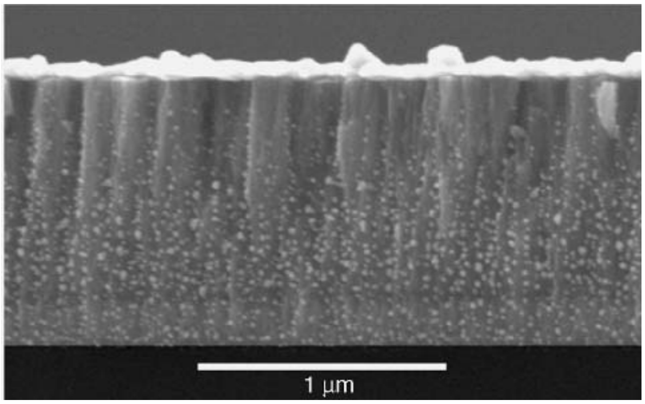

Fig. 3 SEM cross-section image of film SiCAg-5 (36% Ag)

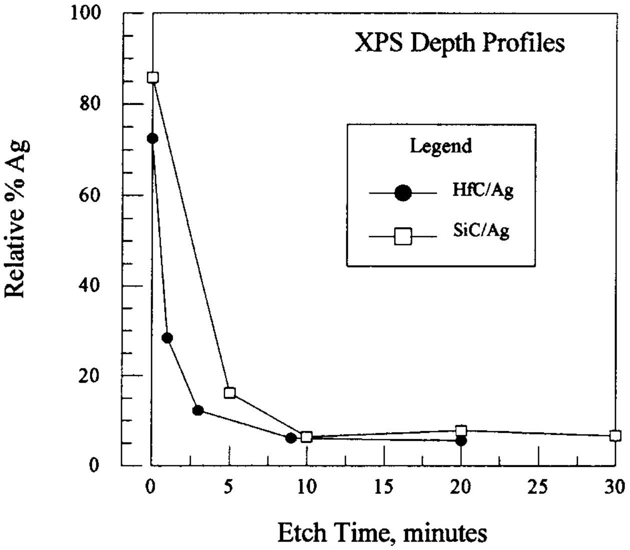

Fig. 4 XPS depth profile results for films SiCAg-5 and HfCAg-5. Both show a strong tendency for Ag segregation to the surface.

XPS depth profiling analysis was conducted of film SiCAg-5, and the results are shown in Fig. 4. The concentration clearly shows a dramatic increase in Ag as the surface is approached. Unfortunately, the actual depth for the data in Fig. 4 is not known because the ion etching rates for a SiC/Ag composite structure are not yet known. However, based on the SEM cross-section images, it is expected that the ion etching has penetrated the highly enriched Ag layer on the surface into the Ag depleted layer below it. Further below this region, SEM showed small particles that are hypothesized to be Ag. With additional ion etching time, it may be possible to observe an increase in Ag concentration due to these particles. Experiments to conduct full depth profiles of these films are currently underway.

The vacuum tribology results for the SiC/Ag films are shown in Fig. 5. In the figure, the data points were determined by averaging the friction coefficient over the entire test of 10 000 cycles, and the error bars show the standard deviation in that data. For SiC films, the average friction coefficient is 0.4, but as the Ag content is increased the friction decreases in a nearly linear manner to a value of 0.13 at 36% Ag. Additional Ag does not reduce friction, as shown in the sample with 50.8% Ag and, in fact, may increase it slightly due to a plowing effect. Nonetheless, the reduction of friction by nearly a factor of four due to Ag additions indicates that these films may be useful in components operating in vacuum environments.

3.2 HfC/Ag Films

The magnetron sputter deposition parameters and relative Ag content for films deposited at 200 °C are shown in Table 2. The power applied to the Ag gun ranged from 0-42 W, and the corresponding Ag concentration from 0-32%. The XRD pattern for the film with the highest Ag content is shown in Fig. 6. In this pattern crystalline peaks from both HfC and Ag are ob-

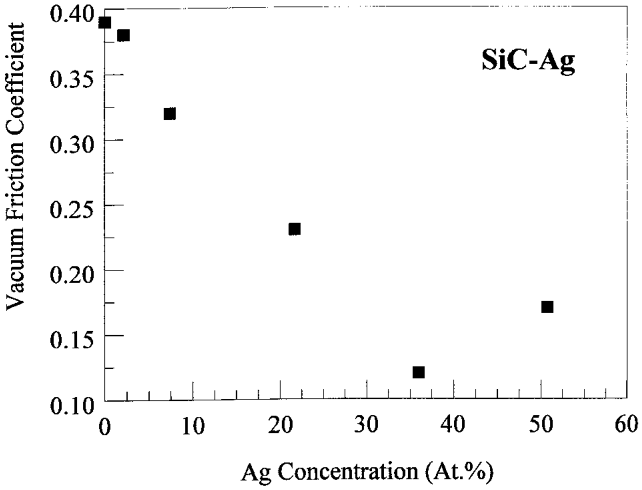

Fig. 5 Average friction coefficient versus percent Ag for films tested in vacuum for 10 000 cycles. A minimum friction coefficient is found at 36% Ag.

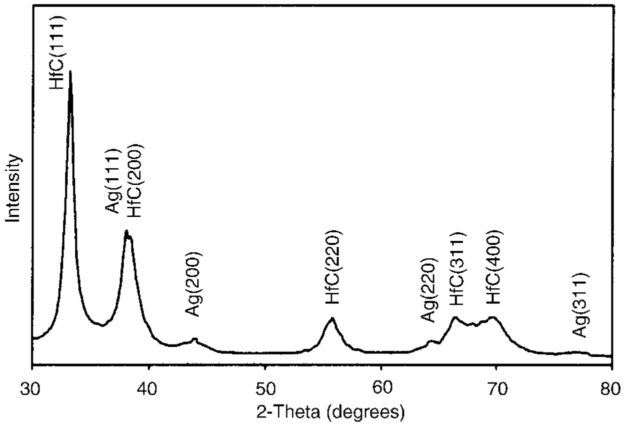

Fig. 6 XRD pattern for film HfCAg-6 (32%Ag). Peaks for both crystalline HfC and Ag are observed in this pattern, indicating phase separation has occurred between these phases.

Table 2 Deposition Parameters and Compositions of the HfC-Ag Films Deposited at 200 °C

Sample	HfC-Gun Power, W	Ag-Gun Power, W	Ag Content Ag/(Ag + Hf), %
HfCAg-1	250	0	0
HfCAg-2	250	10	8.8
HfCAg-3	250	30	17.6
HfCAg-4	250	32	19.5
HfCAg-5	250	35	24.1
HfCAg-6	250	42	32.0

served. In contrast to the SiC/Ag, the HfC has formed with a crystalline structure. For both the Ag and HfC, the largest peak is the (111) reflection, indicating some texture in this orientation, which is common for sputter deposited films based on face-centered-cubic structures.

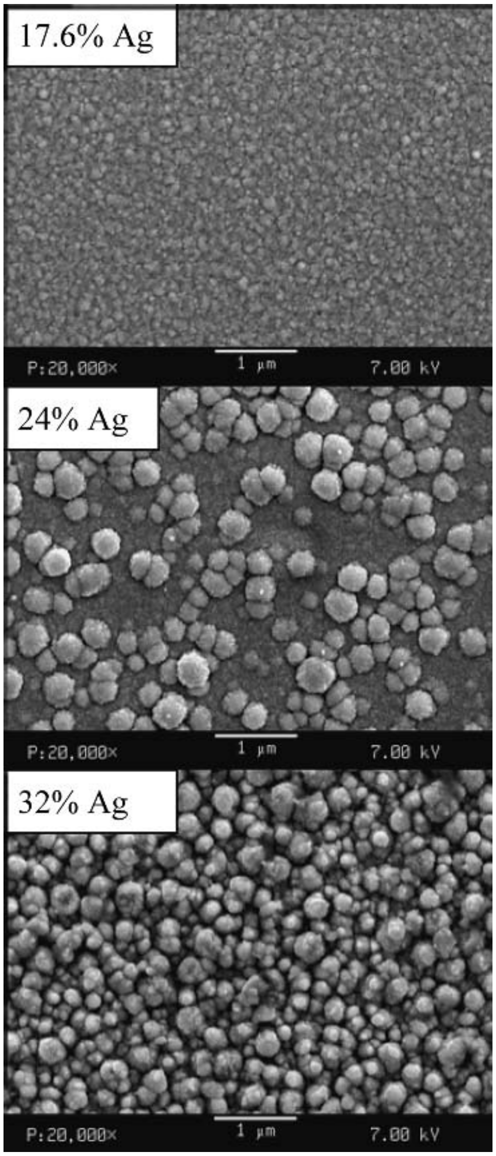

Fig. 7 SEM images of the surface of HfC-Ag films with the concentration of silver indicated. At higher Ag concentrations, nodules of Ag cluster on the surface.

The SEM images of the sample surface for three HfC/Ag films are shown in Fig. 7. In this case, the nodules appear at 24% Ag and increase in density at 32% Ag. A fractured cross-section sample is shown in Fig. 8(a), and while there are some small embedded particles near the substrate, the grain structure of the film dominates the morphology, making it difficult to image the phase structure. Therefore, a polished taper cross-section sample was prepared and examined in the SEM and is shown in Fig. 8(b). This image shows a definite change in structural morphology as the film surface is approached. The small particles near the surface correspond well in size (~0.25-0.33 µm diameter) to those observed in the SEM image of the surface. Therefore, in the HfC/Ag films, it appears that beyond a given Ag concentration, the Ag forms as nodules at or near the surface. XPS analysis was also conducted to further understand the distribution of Ag in these films. Figure 4 shows the

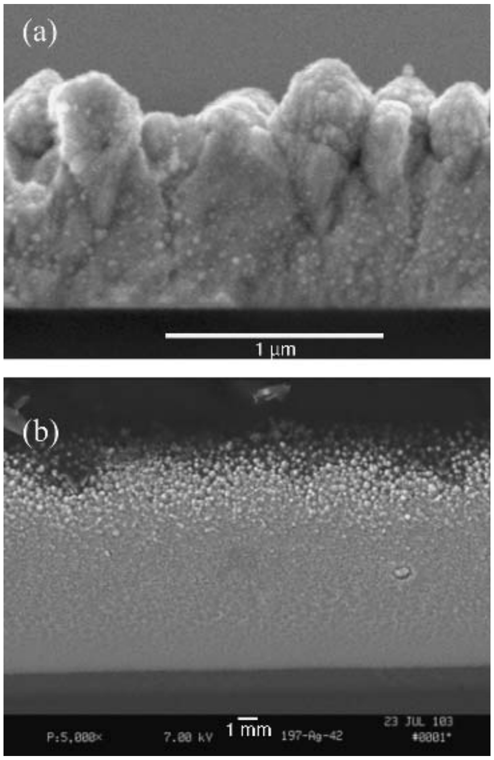

Fig. 8 Cross-section SEM images of sample HfCAg-6 (32% Ag): **(a)** fractured cross section, **(b)** polished and ion-etched cross section

result for film HfCAg-5. As in the case for SiC-Ag film, a highly enriched surface Ag layer is observed.

The vacuum tribology results for the HfC/Ag films are shown in Fig. 9. Again, the data show the average value of the friction coefficient over 10 000 cycles, and the error bars show the standard deviation in that data. For these films, the average friction coefficient can be divided into two plateaus, one at $\mu \approx 0.4$, for the first three films, and another near $\mu \approx 0.2$ for the last three films. This reduction in friction coefficient by a factor of about two is substantial, but less than the factor of four observed for the SiC/Ag films.

4. Discussion

In this study, the structure and vacuum tribological properties of composite SiC/Ag and HfC/Ag films, deposited by magnetron sputtering, have been studied. The concept underlying these coatings is that the free Ag will provide lubrication in vacuum environments while the carbide phase provides mechanical support for the Ag and, therefore, good wear resistance. The first consideration in our experiments is whether the carbide and Ag form separate phases. For the films studied here, as well as in our previous experiments with TiC/Ag and WC/Ag,[7,8] phase separation between the carbide and Ag phases was easily obtained. This is likely due to a large positive heat of mixing in these systems.

The microstructure of the films, particularly the nature of the Ag phase, is expected to have an important influence on the tribological behavior of the films. Ideally, particles ~0.1 µm in diameter, which are uniformly embedded in the carbide film, are envisioned, so that as the film wears a continuous supply of Ag is available to provide lubrication in the wear track. In the present case, a strong tendency for Ag segregation was observed near the film surface, which led to a Ag-depleted region below the surface. Closer to the substrate, some films showed embedded particles that are likely to be Ag. The development of this structure is related to the large positive heat of mixing between Ag and the carbide, as well as the tendency for the Ag to be more surface active (i.e., placing Ag on the surface of the carbide reduces the surface energy). In the present case, it is possible that the Ag diffuses to the surface during deposition, or during cooling after deposition. However, in this system the time required to cool from the deposition temperature of 200 °C to below 100 °C is small compared with the time of deposition. Therefore, it is more likely that the observed film structures evolve during deposition. However, given sufficient time and temperature, ultimately, the equilibrium structure would be a bilayer with Ag on top. Therefore, obtaining the embedded particle microstructure will require judicious choice of deposition parameters, particularly the deposition temperature and Ag concentration. Further studies are needed to understand how the structure evolves during deposition. These studies could involve temperature effects and affect the overall film thickness, as well as diffusion-based models for the structural evolution.

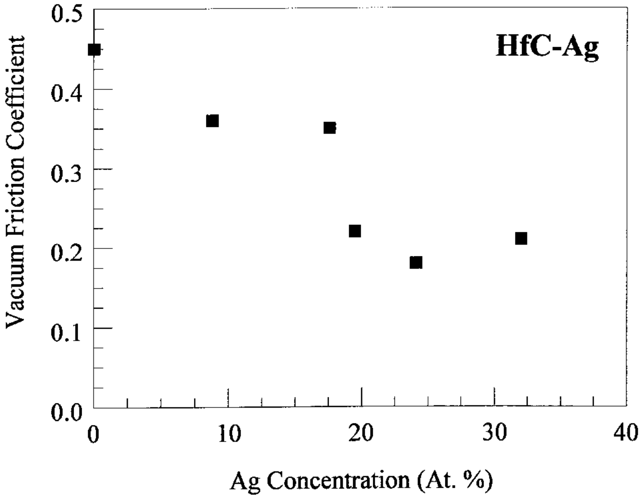

Fig. 9 Vacuum tribology test results for HfC-Ag films. The friction coefficient shown is the average over 10 000 cycles.

Despite not having achieved the desired embedded particle structure, the films showed improvements in vacuum tribological behavior when sufficient Ag was present. The minimum amount of Ag appeared to be ~15% for SiC/Ag and ~25% for HfC/Ag. The existence of a minimum concentration of Ag is due to the need to coat a significant portion of the wear track with Ag, and below this minimum concentration, any Ag present on the surface is swept out of the wear track due to the higher friction caused by the carbide phase. Again, this hypothesis needs to be verified with further experimentation. Also, the success of the films with higher Ag concentrations suggests that envisioned "ideal" microstructure may not be strictly necessary to obtain films that perform well.

5. Conclusions

- Codeposition of HfC-Ag and SiC-Ag at a substrate temperature of 200 °C results in phase separation in the deposited films.
- Microstructural analysis showed that the Ag was nonuniformly distributed within the film. Closer to the substrate, embedded particles of Ag were observed. However, closer to the film surface, there was a region depleted of Ag followed by a surface-rich Ag surface layer.
- XPS analysis verified the chemical segregation of Ag to the film surface.
- Ball-on-flat tribology tests conducted in vacuum showed that Ag additions to the carbide films reduced the average friction if sufficient Ag was present.

Acknowledgment

The financial support of the Air Force Office of Scientific Research under Grant No. F49620-98-1-0499 is gratefully acknowledged.

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