



SYNTHESIS, PROPERTIES AND CHARACTERIZATION OF CR-DLC NANOCOMPOSITE FILMS

Varshni Singh
Ph.D. Candidate

Faculty Advisor: Dr E.I. Meletis

ABSTRACT

Diamondlike carbon (DLC) films have been extensively studied over the past decade, due to their unique combination of properties. One of the drawbacks with DLC films is that they are thermally unstable beyond 350°C [1]. Above 400°C the changes are more profound and graphitization of the film occurs by conversion of C bonds from sp^3 to sp^2 , a phenomenon that is also observed during wear at hot spots [2]. Thus for more than a decade researchers have focused on metal-containing DLC (Me-DLC) films in an effort to improve wear resistance, adhesion, thermal stability and toughness. A number of studies on synthesis and characterization of Me-DLC films have been conducted on Si-, Ti-, Ta-, W- and Nb-DLC [3-10]. Even though Cr is a carbide former and possesses an attractive combination of other properties (corrosion resistance, wear resistance, etc.) little work has been reported in this area [6,11]. The purpose of the present work was to initiate a systematic study of the processing-structure-property relationship in Cr-DLC films as a function of Cr content. The objective is to develop a better understanding of this system and identify possible compositional ranges where tribological performance and thermal stability are significantly improved.

Cr-DLC nanocomposite films were deposited on Si (100) substrate, by reactive magnetron sputtering utilizing an intensified plasma-assisted processing system. The processing parameters (chamber pressure, bias voltage, magnetron current, etc.) were varied to synthesize Cr-DLC films, with Cr content ranging from ~0.1 at. % to 28 at. %. Carbon and chromium content was determined by wavelength dispersive spectroscopy (WDS) utilizing a JEOL JXA 733 super electron probe microscope. X-ray diffraction (XRD) experiments were performed, using a Rigaku Miniflex 2 θ diffractometer with a Cu - K_{α} source and transmission electron microscopy (TEM) was conducted in a JEOL JEM 2010 electron microscope. Pin-on-disc experiments were conducted by utilizing an ISC-200 tribometer and the wear rate was calculated by a Veeco 3D optical profilometer.

Mechanical properties, of the films were studied by nanoindentation measurements, using a Hysitron Triboscope® instrumented nanoindentation/ nanoscratch device incorporated on a Digital Instrument Dimension 3100 atomic force microscope. The short-range order structure of the films is being studied by the xray absorption fine structure (XAFS) spectra collected by using bending magnet radiation at the double crystal monochromator 1 beamline. The thermal stability experiments were conducted by utilizing a DSC-7 differential scanning calorimeter.

XRD patterns of DLC and Cr-DLC films, show that all the films exhibited nearly the same XRD pattern, indicating an amorphous structure. Electron diffraction and high-resolution TEM studies show that the films, with ~ 9 at. % Cr, deposited using low (-200 V) and high (-1000 V) specimen bias during processing are composed of nanocrystalline metallic Cr and nanocrystalline cubic chromium carbide, respectively surrounded by an amorphous matrix. Fig. 1 show the dark contrast clusters, diameter 1 – 5 nm, surrounded by an amorphous matrix corresponding to nanocrystalline Cr carbide. The XANES spectra of the Cr-DLC films show that the Cr content (5 to 28 at. %) in the Cr-DLC films, deposited at -1000 V bias, has little effect on its structure and Cr atoms are incorporated in the carbon network. This initial result is in agreement with that of the TEM results. Furthermore, such preference for metal atoms to be incorporated into the local carbon structure has also been shown by our recent XAFS experiments on Si-DLC films with ~10 at. % Si [12].

Fig. 2 presents the variation of the coefficient of friction (μ) and wear rate of Cr-DLC films (deposited at -1000 V) with Cr content. The results in Figs. 2 show that in general all Cr-DLC films exhibit a low μ (less than 0.2) for both alumina and 440 stainless steel pins. It is interesting to note that μ remains at low levels (less than 0.15) for up to a Cr/C ratio of 0.24. At a higher Cr level, the results indicate that the coefficient of friction increases. Very similar behavior has been observed previously for W-DLC films [5]. The wear rate was also found to be relatively independent of

pin material. The wear rate was low and remained at almost the same levels in films with a Cr/C ratio less than 0.24. At higher Cr content (Cr/C equal to 0.35), the wear rate increased significantly (by at least an order of magnitude), which is consistent with the relatively higher μ observed for that film. The present results are in general agreement with the previous reports however, doesn't show high wear rates at very low Cr content.

The DSC result qualitatively suggests that the thermal stability of the Cr-DLC films increases with increasing Cr content, due to stabilizing effect of Cr on the DLC matrix network, up to the point where the DLC network is completely stabilized. Nanoindentation results suggest that the hardness of the films reduces with increasing Cr content to ~3 atomic % and then it stabilizes around 13 GPa. With the exception of an initial deep, reduced modulus ($E/(1-\nu^2)$) increases with increasing Cr content and stabilizes around 118 GPa at ~11 atomic % Cr. The $H/E/(1-\nu^2)$ exhibits a peak value of ~0.17 at 0.05 atomic % Cr and then gradually decreases and stabilizes to values around 0.11. Compared to other Me-DLC films, the present profile of $H/E/(1-\nu^2)$ for Cr-DLC exhibits this interesting region yet to be explored between 0.05 at. % Cr and ~2.75 at. % Cr. Presently, the reason for this peculiar behavior is unknown.

At present, the in-depth analysis of the spectra obtained from Cr-DLC films is underway. Study of Cr-DLC films deposited at lower substrate bias is planned for the next period. In addition, a couple more compositions in the aforementioned range between 0.05 at. % Cr and 2.75 at. % Cr are planned to explore the lower range of the Cr content. So as to completely understand the effect of Cr content and the substrate bias on the short-range order around Cr in the Cr-DLC films further analysis and experiments are underway.

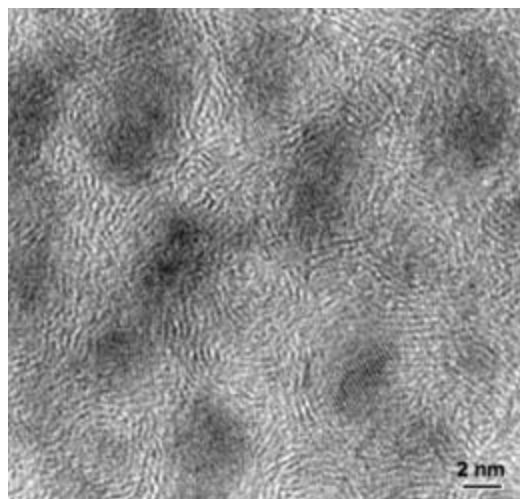


Figure 1 HRTEM image of Cr-DLC films with Cr 9 at. % deposited at a bias of -1000V.

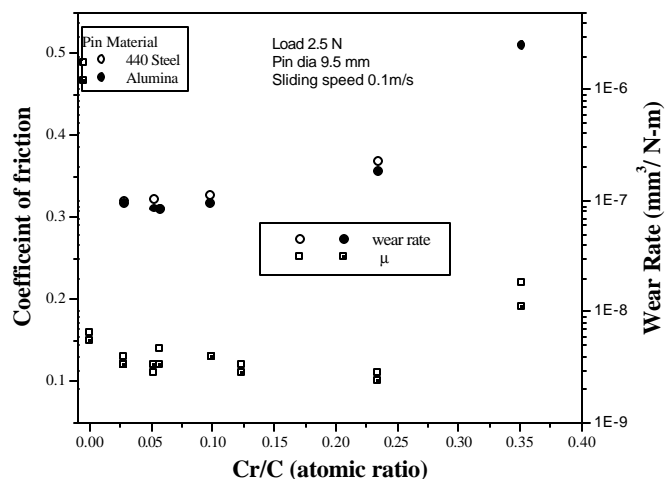


Figure 2 Coefficient of friction and wear rate of Cr-DLC films of Cr/C ratio.

ACKNOWLEDGMENTS

This work was supported by the Army Research Office grant DAAG55-98-1-0279 and Louisiana Board of Regents. TEM was performed at MCC facility of LSU with the help of Dr J. Jiang. Nanoindentations were performed with the help of Ms Tracy Morris and XAFS spectroscopy was done with the help of Dr V. Palshin and Dr R. Tittsworth in CAMD, LSU. WDS was performed using electron microscopy facility of the Geology Department at LSU with the help of Dr. Xie. Assistance of Mr. Pankaj Gupta in the deposition experiments is also acknowledged.

REFERENCES

1. Z.L. Akkerman, H. Efstathiadis, and F.W. Smith, *J. Appl. Phys.*, **80**(5), 3068-3075 (1996).
2. Y.Liu and E.I. Meletis, *J. Mater. Sci.*, **32**, 3491 (1997).
3. A. Varma, V. Palshin, K. Fountzoulas and E.I. Meletis, *Surface Engineering* **15**(4), 301-306 (1999).
4. K. Oguri and T. Arai, *J. Mater. Res.*, **7**(6), 1313 (1992).
5. C.P. Klages and R. Memming, *Materials Science Forum*, **52-53**, 609-644 (1989).
6. Y.L. Su and W.H. Kao, *J. Mater. Eng. Perf.*, **9**(1) (2000) 38-50.
7. M. Fryda, K. Taube and C-P Klages, *Vacuum*, **41**(4-6) (1990) 1291-1293.
8. H. Dimigen and GP Klages, *Surf. Coat. Technol.*, **49** (1991) 543-547.
9. W.J. Meng and B.A. Gillispe, *J. Appl. Phys.*, **84**(8) (1998) 4314-4321.
10. K. Bewilogua, C.V. Cooper, *Surf. Coat. Technol.*, **132** (2000) 275-283.
11. X. Fan, E.C. Dickey, S.J. Pennycook and M.K. Sunkara, *Appl. Phys. Lett.*, **75**(18) (1999) 2740-2742.
12. V.A. Palshin, R.C. Tittsworth, K. Fountzoulas and E.I. Meletis, *Journal of Materials Science* **37**, (2002).