

PREPARATION, STRUCTURE AND MECHANICAL PROPERTIES OF NANOSTRUCTURED COPPER-CARBON FILMS *

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Received: April 29,2003

Abstract. Pure copper and copper-carbon composite films have been deposited on silicon substrates by sputtering of a copper target associated with microwave plasma-enhanced chemical vapor deposition process of carbon from argon-methane mixtures of various compositions. The composition of films was determined by Rutherford backscattering spectroscopy (RBS) and Raman spectroscopy. The morphology of the surface and cross-section of samples was examined by scanning electron microscopy. The crystallographic structure was identified by x-ray diffraction techniques. The electrical resistivity of films was obtained by four point probe measurements. These composite films consisted of polycrystalline copper and amorphous carbon phase. The copper crystallite size was in the range 15-30 nm and less than 5 nm for a carbon content in Cu-C films ranging from 20 to 25 at. % and from 60 to 75 at. %, respectively. The electrical resistivity of Cu-C films containing 20 to 25 at. % of carbon was approximately $2.5 \mu\Omega \text{ cm}$ whereas the resistivity value can reach $10^7 \mu\Omega \text{ cm}$ for films containing 60 to 75 at. % of carbon. A large variation of grain size and electrical resistivity of nanostructured Cu-C composite thin films was noticed as the CH_4 concentration in the gas phase was varied from 60 to 70 %. The hardness and Young modulus of films were deduced from nanoindentation measurements. The friction coefficient of films was determined by pin-on-disk tribological tests conducted under various conditions. The deposition rate, composition, morphology, structure, electrical resistivity, mechanical properties and friction properties of films were investigated as functions of the methane concentration in the gas phase or carbon content in the Cu-C composite films.

* Presented at NATO Advanced Research Workshop on Nanostructural Materials and Coatings for Biomedical and Sensor Applications, Kiev, August 4-8, 2002

1. INTRODUCTION

Amorphous carbon films such as diamond-like carbon (DLC), hydrogenated amorphous carbon (a-C:H) and i-C films produced by carbon ion beam deposition exhibit outstanding properties, in particular high hardness and elasticity. These films providing low friction coefficients and reduced wear rates for sliding tests conducted under various conditions are very attractive for tribological applications [1]. However, the magnitude of compressive residual stresses developed in these films may reach very high values (several GPa); as a result, the adhesion of amorphous carbon films on various substrates, in particular on stainless steel is not suffi-

cient to ensure the reliability required for mechanical components in industrial applications. In addition, the thermal stability of these films is relatively low (these films cannot operate at temperatures higher than 250 °C) and the friction coefficient increases as the relative humidity (RH) in the environment increases. For instance, the friction coefficient for a sliding contact between DLC and stainless steel was observed to increase progressively from 0.05 in dry air up to 0.3 for RH of 100 % [2].

Recently, novel materials have been proposed to overcome these difficulties, in particular DLC nanocomposite or DLN films composed of amorphous carbon (DLC or a-C:H) and a-Si:O vitreous phase [3,4]. The hardness of these DLN films be-

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tween 12 and 17 GPa is less than the hardness of DLC films (15 to 25 GPa). However, the residual stresses are significantly lower (0.5 to 1 GPa) and these DLN films were found to be tightly adherent to various types of substrates.

The objective of the present research program is to prepare nanostructured metal-amorphous carbon films exhibiting tribological properties similar to those of DLC nanocomposite (DLN) films. Metals such as Cu, Ni or Ag not miscible with carbon and not converted into carbide phase are very attractive candidates. In these metal-carbon composite films, nanocrystallites of metal would be wrapped in the matrix of amorphous carbon which acts as a tissue surrounding the metal crystallites. The metal-carbon interfaces are expected to be very abrupt and the migration of dislocations in the metal grains would be negligible. Therefore, these nanostructured Cu-C composite films would exhibit a relatively high hardness (and reduced wear rate) as the load is applied perpendicularly to the surface and a relatively low shear modulus (and reduced friction coefficient) as the load is applied in the direction parallel to the surface of films. For tribological tests, the amorphous carbon phase separating the metal crystallites from each other may act as a solid lubricant and the friction strength between two adjacent metal crystallites in relative sliding motion may be considerably reduced.

For the present work, copper was selected among various other metals such as Ni, Co, Ag or Au as a not miscible element with carbon. The technique used for deposition of nanostructured copper-amorphous carbon (nc-Cu/a-C:H) composite films consisted of a combination of two microwave plasma-assisted deposition processes, namely plasma-enhanced chemical vapor deposition (PECVD) process of carbon from argon-methane mixtures associated with sputter deposition of copper from a copper target. This deposition technique was based on a distributed electron cyclotron resonance (DECR) microwave plasma reactor [5]. The composition of films was determined by Rutherford backscattering spectroscopy (RBS) and Raman spectroscopy. The crystallographic structure of films was analyzed by x-ray diffraction techniques. The grain size of copper incorporated in the amorphous carbon matrix was investigated as a function of the composition of the gas phase and carbon content in the films. The microhardness of films measured by nanoindentation and the friction coefficient determined by pin-on-disk tribological tests were also investigated as functions of the methane concentration in the gas phase and carbon content in the films.

2. EXPERIMENTAL PROCEDURE

Copper-carbon composite films have been deposited on (100)-oriented single crystal silicon substrates mounted on a water-cooled substrate holder. The deposition of films was carried out using a new plasma reactor based on multipolar magnetic confinement, named as distributed electron cyclotron resonance (DECR) microwave plasma [5]. The cylindrical reaction chamber of 280 mm in diameter was made of stainless steel (Fig. 1). The microwave field applicator consisting of a linear conductor of cylindrical cross-section (8 mm in diameter), called as antenna, was placed a few millimeters far from the grounded reactor wall. Permanent magnets contained within grounded casings of rectangular cross-section provided the 875 Gauss isomagnetic surface in the vicinity of the antenna along its entire length of 250 mm required for ECR conditions at a 2.45 GHz excitation frequency. The plasma reactor was equipped with four antennae placed at the periphery of the deposition chamber. The microwave power on each antenna could be adjusted from 0 to 200 W. For deposition of films, the total microwave power was 400 W. The d.c. voltage applied to the copper target of 100 mm in diameter was maintained at 300 V. The current intensity collected by the copper target varied from 0.25 to 0.15 A as the CH₄ concentration in the gas phase varied from 0 to 100 %. As a result, the sputtering power was in the range from 45 to 75 W. The substrate holder at 13

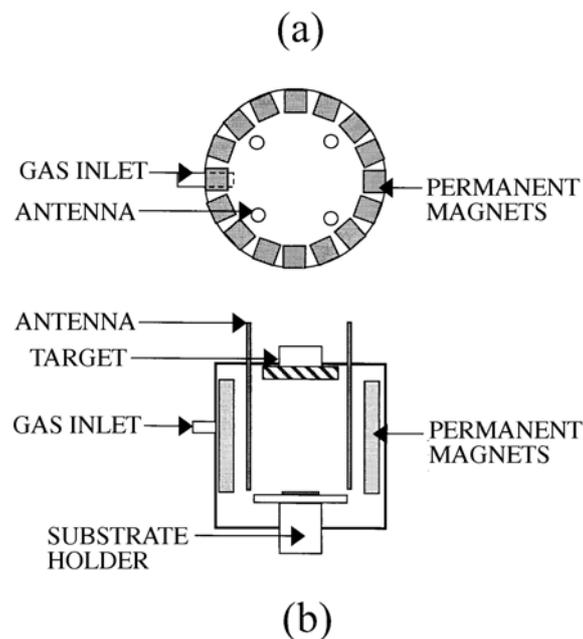


Fig.1. Schematic drawing of the DECR microwave plasma reactor : (a) top view, (b) cross-section view.

cm far from the target was maintained at the floating potential. Prior to the gas phase ionization, the total pressure in the reactor was fixed at 0.13 Pa while the CH₄ concentration in the gas phase was varied from zero to 100 %. The maximum flow rate of pure argon and methane required for a total pressure of 0.13 Pa in the deposition chamber was 8 and 6 cm³/min, respectively. After deposition, the films were maintained in argon under a pressure of 0.13 Pa during one hour for complete cooling down to room temperature before taking off and exposure of samples to room air.

The thickness of films was measured by surface profilometry. The deposition rate of films was deduced from the thickness of films produced for a given deposition time generally fixed at 30 min. The composition and mass density of films were obtained from RBS measurements using α particles of 2 MeV or protons of 1 MeV depending on the film thickness; the incidence and detection angles were 90° and 160°, respectively. The depth concentration profile of oxygen atoms was determined by ¹⁶O(d, α)¹⁴N nuclear reaction analyses (NRA) using a deuteron beam of 900 keV. The films were also analyzed by Raman spectroscopy at room temperature using Spex 1403 spectrometer with a photomultiplier tube R828 cooled down to 243K. An argon ion laser beam at a wavelength of 488 nm performed the excitation with a power on the sample of 0.3-0.35 W.

The surface and cross-section of films deposited on Si substrates were examined by scanning electron microscopy (SEM). The crystallographic structure of films was investigated by x-ray diffraction (XRD) techniques using an Inel diffractometer in θ -2 θ position, with a collecting angle varying from 5 to 120° and the usual copper K _{α 1} radiation ($\lambda = 1.5406 \text{ \AA}$). The position and the integral width of x-ray diffraction peaks were determined to identify the crystalline phase and to calculate the grain size from Scherrer equation: $\beta_{2\theta} = \lambda / (L \cos \theta)$; in this equation, $\beta_{2\theta}$ is the integral width of a given (hkl) diffraction peak at 2 θ angle, λ the wavelength of the incident copper K _{α 1} radiation, L the size of crystallites in the (hkl) direction and θ the Bragg angle.

The sheet resistance of films deposited on Si substrates was determined by four point probe measurements and the electrical resistivity deduced from the sheet resistance and film thickness was investigated as a function of the CH₄ concentration in the gas phase or carbon content in the films.

The mechanical properties of films were determined by nanoindentation using a Nano Indenter II equipped with a Berkovich indenter. The load was varied in the range of 0.25-50 mN. The hardness

and modulus of elasticity were found at the minimal load using Oliver and Pharr model [6]. The average indentation contact pressure (Meyer hardness) was found by the method proposed by Dub *et al.* [7]. The pin-on-surface tribological tests were carried out by means of TAY-1M tribometer with a pin made of BK-8 hard alloy (hardness of 87.5 HRC). The sliding speed was maintained at 4 mm/s. The load was either 0.5 or 1 N.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Deposition rate and composition of films

Pure copper and carbon containing copper films have been deposited on Si substrates covered with a native oxide layer under various experimental conditions. These films of 0.1 to 0.5 μm in thickness tightly adherent to Si substrates exhibited a shiny surface. The visual aspect of films gradually changed from the reddish color of copper to dark red or black color as the carbon content in the films increased from 0 to 75 at. %.

The deposition rate of Cu-C films was dependent on the CH₄ concentration in the gas phase (Fig.2). For pure copper films, the deposition rate was approximately 260 $\text{\AA}/\text{min}$. The deposition rate of Cu-C films decreased very slowly from 260 to 210 $\text{\AA}/\text{min}$ as the CH₄ concentration in the gas phase increased up to 50 %. The minimum value of the deposition rate of 140 $\text{\AA}/\text{min}$ was reached for Cu-C films produced from Ar-CH₄ mixtures containing 60 % of methane. For higher CH₄ concentrations, the deposition rate of films increased progressively with increasing CH₄ concentration and can reach approximately 160 $\text{\AA}/\text{min}$ for films produced from pure CH₄ microwave discharges.

The concentration of copper and carbon atoms in the films determined by RBS measurements was found to be dependent on the CH₄ concentration in the gas phase (Fig.2). Pure copper films were produced from pure argon microwave discharges. The argon content in pure copper and Cu-C films was less than the detection limit (1 at. %) of RBS analyses. The carbon content reached 20 at. % (and the copper content was 80 at. %) in Cu-C films deposited from Ar-CH₄ mixtures containing 10 % of methane. The carbon content in the films increased slightly from 20 to 25 at. % (and the copper content decreased from 80 to 75 at. %) as the CH₄ concentration in the gas phase increased from 10 to 60 %. The increase in CH₄ concentration in the gas phase

Table 2. Data obtained from mathematical treatments of Raman spectra of Cu-C films produced from argon-methane mixtures of various compositions.

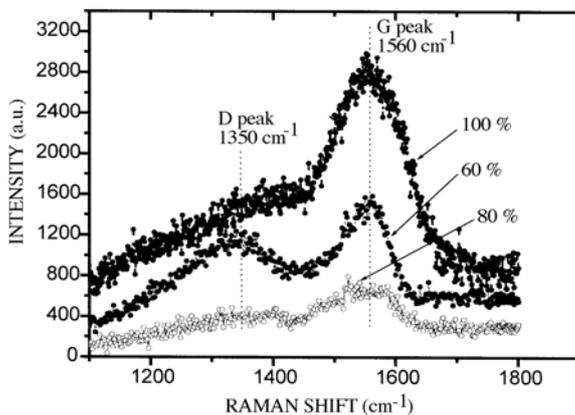
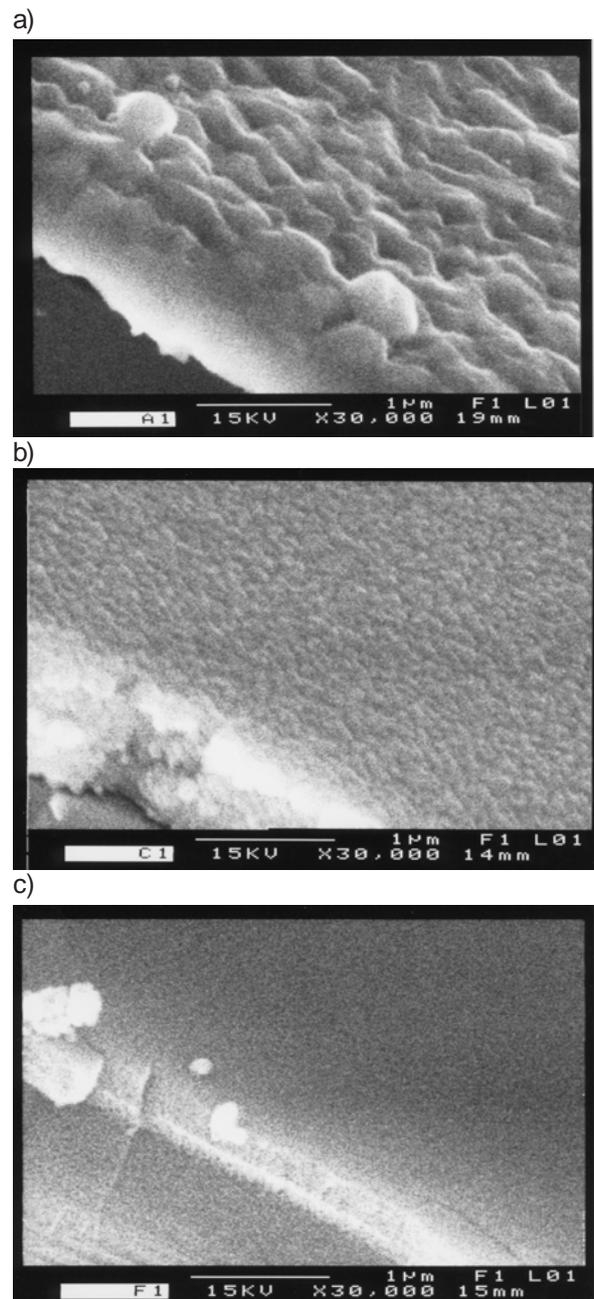
CH ₄ concent. (%)	Carbon content (at.%)	D peak (cm ⁻¹)	G peak (cm ⁻¹)	FWHM of D peak (cm ⁻¹)	FWHM of G peak (cm ⁻¹)	I _D /I _G ratio
60	25	1337	1551	170	101	1.25
80	65	1357	1560	228	106	1.13
100	75	1350	1557	280	135	0.71

A comparative analysis of the spectrum parameters obtained from Cu-C composite films with those given in the literature for the size of carbon clusters [9] enables one to state that the Cu-C films containing 25 at.% of carbon deposited with a CH₄ concentration of 60% has a greatest degree of dimensional heterogeneity of carbon atoms clustered.

3.2. Morphology, crystallographic structure and electrical resistivity of films

The morphology of the surface and cross-section of pure copper and Cu-C films was examined by scanning electron microscopy (Fig.4). Pure copper films exhibited a relatively rough surface. The surface roughness decreased progressively as the carbon content in the films increased.

Typical XRD patterns and XRD data for films produced from Ar-CH₄ mixtures of various compositions are given in Fig.5 and Table 1, respectively. The XRD pattern of pure copper films produced by sputtering exhibited only the diffraction peaks corresponding

**Fig.3.** Typical Raman spectra of Cu-C films produced from argon-methane mixtures of various methane concentrations. The carbon content in these films is given in Table 2.**Fig.4.** SEM micrographs of : (a) pure copper film, (b) Cu-C films containing 25 at.% of carbon and (c) Cu-C film containing 75 at.% of carbon.

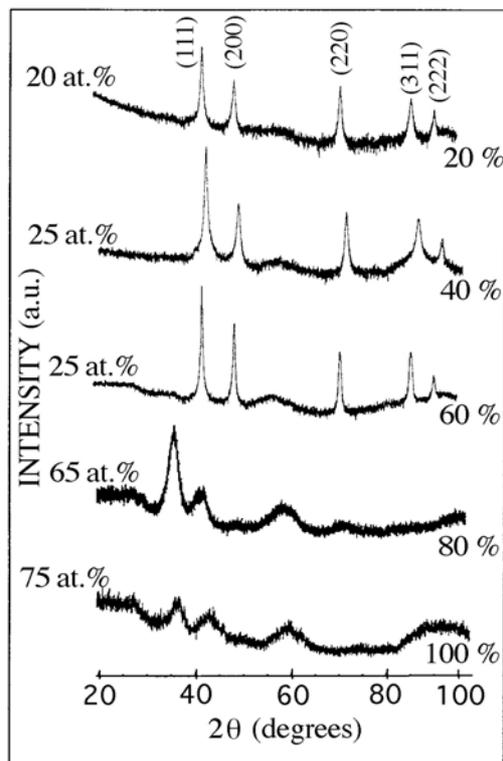


Fig.5. Typical X-ray diffraction patterns of Cu-C films of various carbon contents produced from argon-methane mixtures of various methane concentrations. The (hkl) Miller indices are those of the f.c.c. Cu phase.

to those of the face centered cubic (f.c.c.) copper phase (Table 1). The relative peak intensities and the position of diffraction peaks in the XRD pattern were very similar to those reported in the JCPDS card [10]. As a result, neither a preferential crystallographic orientation nor variation of the crystal lattice parameter was detected for these sputter-deposited copper films. Therefore, these films consisted of polycrystalline copper and amorphous carbon phase with various metal and carbon concentrations. The position of diffraction peaks in the XRD patterns was independent of the CH_4 concentration in the gas phase; as a result, the crystal lattice parameter of the copper phase was constant and independent of the composition of Cu-C films. However, the intensities and widths of diffraction peaks were found to be dependent on the CH_4 concentration in the gas phase, i.e., composition of films. Depending on the carbon content in the Cu-C films, two types of films can be distinguished on the basis of XRD data. For films containing less

than 25 at. % of carbon produced from Ar- CH_4 mixtures with a CH_4 concentration below 60 %, the XRD patterns were similar to that of pure copper reported in the JCPDS card. A number of diffraction peaks corresponding to the f.c.c. copper phase were not detectable in the XRD patterns of Cu-C films containing more than 55 at. % of carbon produced from Ar- CH_4 mixtures with a CH_4 concentration higher than 70 % (Table 1). In addition, the diffraction peaks broadened progressively as the carbon content in the Cu-C films increased. For instance, the XRD pattern of Cu-C films produced from pure CH_4 microwave discharges exhibited only the (111) diffraction peak ascribable to the f.c.c. copper phase.

Additional diffraction peaks can be detected in XRD patterns of few Cu-C films containing more than 50 at. % of carbon. These diffraction peaks appearing for 2θ angles of 36.1, 42.4 and 61.5° (for example, in the XRD pattern of Cu-C films produced from pure methane microwave discharges given in Fig.5 can be attributed to the (111), (200) and (220) diffraction peaks of the cubic copper oxide phase, Cu_2O [11]. Analyses of these samples by RBS and NRA revealed that this oxide formed in the near-surface region of films exposed to room air.

For Cu-C films produced from Ar- CH_4 mixtures with a CH_4 concentration lower than 60 %, the copper grain size determined from the integral width of the (111) diffraction peak and the electrical resistivity of films were in the range 150-300 Å and 2 to 100 $\mu\Omega$ cm, respectively (Fig.6). A large variation of grain size and electrical resistivity was observed as the CH_4 concentration in the gas phase was increased from 60 to 70 %, i.e., as the carbon content in the films increased from 25 to 60 at. %. After this transition, for CH_4 concentrations higher than 70 % or carbon content in the films in the range 60-75 at. %, the copper grain size was lower than 50 Å and

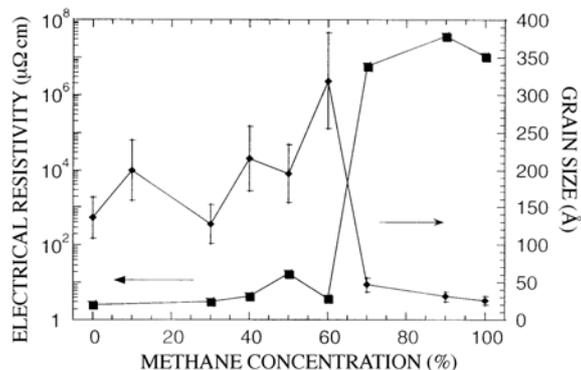


Fig.6. Electrical resistivity and grain sizes of copper for films produced with various methane concentrations in the gas phase.

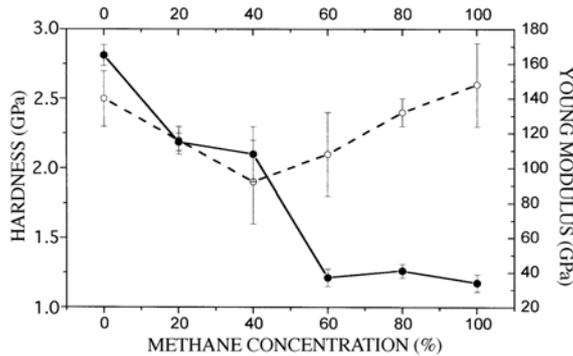


Fig.7. Nanohardness (curve in dashed line) and Young modulus (curve in solid line) of films produced with various methane concentrations in the gas phase.

the electrical resistivity was stabilized in the range 7×10^6 to $3 \times 10^7 \mu\Omega \text{ cm}$. Both the carbon atoms incorporated in the films and the reduced grain size contribute to the increase in electrical resistivity of Cu-C films. These Cu-C films produced from Ar-CH₄ mixtures containing more than 70 % of CH₄ consisted of nanosized copper crystallites (40 to 30 at. % in the films) dispersed through an amorphous carbon matrix (60 to 70 at. % in the films).

3.3. Mechanical and tribological properties of films

The hardness and elastic properties of Cu-C composite films were found to be dependent on the methane concentration in the plasma or carbon content in the films (Fig.7). The hardness varied from 2.5 to 1.9 GPa with increasing methane concentration up to 40 %; then, the hardness increased from

1.9 to 2.6 GPa as the methane concentration increased from 40 to 100% in the gas phase. The magnitude of the Young modulus of composite films decreased from 160 to 30 GPa with increasing methane concentration in the plasma or carbon content in the films.

The results of tribological tests of Cu-C films with various compositions are displayed in Fig.8. The friction coefficient is observed to be dependent on the sliding distance; in this diagram, three different regions can be distinguished on the basis of the examination of wear tracks in the films by optical methods. A pure Cu film deposited on Si substrate can be considered as a reference sample (Fig.8 (a), curve B). For a sliding distance varying from 0 to 4 m where the friction coefficient increases nearly linearly with increasing sliding distance, the indenter friction occurs only in the Cu film. Assuming that the film has a uniform hardness depth distribution and the indenter does not change its form while rubbing, the increase in the friction coefficient may be attributed to a gradual increase in the real contact area [12]. While rubbing the indenter in the film itself, then a quicker film wear means a quicker growth of the real contact area and, accordingly, a quicker increase in the friction coefficient with increasing the sliding distance. A transition region from 4 to 6 m corresponds to the indenter friction both in the Cu film and on a very smooth Si surface. In the region from 6 m and higher sliding distances, a great variation in the magnitude of the friction coefficient can be observed and corresponds to the penetration of a greater part of the indenter into the substrate.

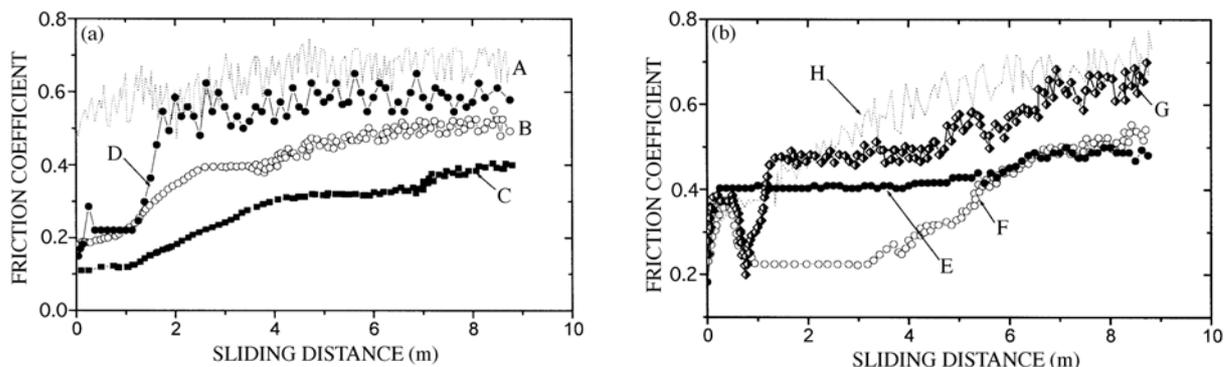


Fig.8. Friction coefficient versus sliding distance of various samples : (a) curve A : bare Si substrate; curve B : pure Cu film on Si substrate; curve C : Cu-C film (20 % of CH₄, 20 at.% of C); curve D : Cu-C film (40 % of CH₄, 25 at.% of C); (b) curve E : Cu-C film (60 % of CH₄, 25 at.% of C); curve F : Cu-C film (80 % of CH₄, 65 at.% of C); Cu-C films (100 % of CH₄, 75 at.% of C); curve G : pure a-C film produced by PECVD from pure methane.

The wear resistance of Cu-C films is worse for carbon contents higher than 60 at.% and for copper grain sizes of less than 5 nm (Fig.8). The best wear resistance was obtained for Cu-C films containing approximately 20 at. % of carbon with a maximum copper grain sizes of 20 nm (Fig. 8(a), curve C). These films studied by Raman spectroscopy were shown to possess the maximum disordering degree (I_D/I_G peak intensity ratio) of graphite clusters. The comparison between the tribological behavior of pure copper and Cu-C films reveals that the major improvement of friction properties in terms of friction coefficient and wear rate is obtained from Cu-C films containing 20 to 25 at.% of carbon. However, the friction coefficient and wear rate of these films are still relatively high with respect to data given in the literature for DLC films.

4. CONCLUSION

Nanostructured copper-carbon composite films consisting of nanosized metal crystallites embedded in an amorphous carbon matrix have been deposited on Si substrates using a distributed electron cyclotron resonance (DECR) microwave plasma reactor. This deposition technique consisted of a microwave PECVD process of carbon from Ar-CH₄ mixtures associated with sputter deposition of metal from a copper target.

The composition, crystallographic structure and electrical resistivity of Cu-C films were observed to be stable as the CH₄ concentration in the gas phase was varied from 10 to 60 %. A large variation of the characteristics of Cu-C films occurred as the CH₄ concentration increased from 60 to 70 %. The origin of this transition was not totally understood for this preliminary investigation of the dual deposition process. For CH₄ concentrations higher than 70 % in the microwave discharge, the nanostructured Cu-C films exhibited anew relatively stable characteristics. The variation of the nanohardness and Young modulus reveal that the elastic deformation and ductility of Cu-C films increase with increasing carbon content. The tribological behavior of films is not yet fully satisfactory. The friction coefficient and wear rate of the Cu-C films are still relatively high at this preliminary stage of the research program. Addi-

tional measurements regarding in particular, the microstructure, morphology, nanohardness and tribological properties of Cu-C films are in progress.

ACKNOWLEDGEMENTS

The authors wish to thank J.J. Grob for RBS measurements and nuclear reaction analyses as well as L. Ortega for XRD analyses of samples. The partial financial support of this research project by NATO Scientific and Environmental Affairs Division, Brussels, Belgium from a Collaborative Linkage Grant is gratefully acknowledged.

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