Interfacial adhesion and toughness of nanostructured diamond coatings

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(Received 10 September 1999; accepted 16 February 2000)

Microwave plasma chemical vapor deposition was used to deposit ultrasmooth nanostructured diamond films (roughness of 14 nm) on a titanium alloy (Ti–6Al–4V) by employing a feedgas mixture containing a high methane fraction (15% by volume) in nitrogen and hydrogen. Of particular interest in this study is the exceptional adhesion of the 4-μm-thick diamond coatings to the metal substrates as observed by indentation testing up to 150 kg load with a ⅛-in.-diameter tungsten carbide ball. No film delamination was observed up to 150 kg indentation load for each of 5 samples grown under the same processing conditions. Scanning electron microscopy of the film surrounding the indentations revealed circumferential microcracking beginning at loads ranging from 60 kg to as high as 150 kg. The strain to cause film microcracking was estimated from calculations of indentation surface areas to be as high as 1.9 ± 0.2%, which represents a significant improvement in toughness over other ceramic coatings.

Much interest has been generated recently in the chemical vapor deposition (CVD) of nanocrystalline diamond films in which the diamond grain size typically ranges from 3 to 30 nm and the surface roughness is about 15 to 40 nm. These films have been produced from a variety of feed gas mixtures including the use of fullerenes or methane in argon (with and without hydrogen), as well as from methane/nitrogen plasmas.[1–3] Although these films have been well characterized with respect to their structure and field-emission properties, surprisingly little information is published on the deposition of nanostructured diamond coatings on metals in which the issues of interfacial adhesion and film toughness are relevant for tribological applications. In this report, we characterize these mechanical properties for nanostructured diamond films grown on a titanium alloy using a feed gas mixture involving an unconventionally high methane fraction (15% by volume) in nitrogen and hydrogen. These films have previously been characterized as containing nanocrystalline diamond grains imbedded in a primarily tetrahedrally coordinated amorphous carbon network and have been shown to exhibit a hardness value of up to 90% that of natural diamond.[4,5] We find that the low root-mean-square (rms) surface roughness of 14 nm along with excellent interfacial adhesion, film toughness, and hardness makes these nanostructured coatings prime candidates for tribological applications.

Circular substrates of 7-mm-diameter and 1-mm-thickness titanium alloy (Ti–6Al–4V) were prepared by a polishing sequence starting with SiC paper of 400 grit, 800 grit, and 1200 grit, followed by napped cloths charged with 3-μm diamond solution and then with 0.3-μm alumina solution. This resulted in an average rms surface roughness of 10 nm for the titanium alloy before deposition. The final preparation step involved seeding for 50 min in a 1–2-μm aqueous diamond powder solution in an ultrasonic bath, followed by rinsing and cleaning in water. Five diamond films were deposited using microwave plasma-assisted CVD with the following conditions: 125-torr chamber pressure, 750–830-W microwave power, 825 ± 25 °C substrate temperature, and gas-flow rates of 500 sccm H_2, 88 sccm CH_4, and 8.8 sccm N_2. The five samples were grown under identical processing conditions in order to investigate the variation in the physical and mechanical properties of the nanostructured films. The average thickness of the five films as measured by pyrometric interferometry[6] was 4.0 ± 0.4 μm and the rms surface roughness was 14 ± 1 nm. The films were characterized by micro-

Raman spectroscopy, x-ray diffraction (XRD), and scanning electron microscopy (SEM), and were found to be nearly identical in structure as those published elsewhere for films grown under similar conditions.[4,5] Table I gives the average and standard deviation of several characterization parameters described in this work.

Each film was indented at loads of 30, 60, 100, and 150 kg using a Rockwell indenter equipped with a ⅛-in.-diameter tungsten carbide ball. Figure 1 shows an optical micrograph of one typical set of indentations. None of the five coatings showed any sign of film delamination up to the highest load tested of 150 kg. The spherical indenter leaves an impression that can be characterized with radius r and depth h as shown schematically in Fig. 2. The initial preindented circular surface area A_i is given by

$$A_i = \pi r^2 \quad . \tag{1}$$

After indentation, this initial area A_i is stretched to a spherical section A_f given by

$$A_f = 2\pi rh \quad . \tag{2}$$

The uniform strain in the film ϵ_f due to the indentation is

$$\epsilon_f = (A_f - A_i)/A_i \quad . \tag{3}$$

The strains in the five films of this study were similar for a given indentation load as shown in Fig. 3.

The film appears to be very well adhered to the metal substrate even in the presence of significant thermally induced residual stress. The average stress of the five films was 5.5 ± 0.6 GPa as measured by the Raman shift of the zone-center optical phonon of cubic diamond.[7] The thermal stress predicted from theory in which the same substrate temperature is assumed and in which the values of Young's modulus and Poisson's ratio for crystalline diamond (1050 GPa and 0.07, respectively) are used is 6.3 GPa.[7] However, it should be noted that previous nanoindentation measurements of our nanostructured diamond films grown at the same processing conditions yielded Young's modulus and hardness values that were 67% and 90%, respectively, those of natural diamond.[4] Because thermal stress is directly proportional to Young's modulus, the stress for our nanostructured diamond films is expected to be less than that of diamond coatings that are nearly 100% crystalline. Grazing-angle XRD analysis of nearly 100% crystalline diamond films compared with the nanostructured diamond films reveals that the nanostructured diamond films have about 48% relative diamond crystallinity. The noncrystalline composition of the nanostructured film is believed to be primarily tetrahedral-coordinated amorphous carbon with small sp^2-bonded clusters. The amorphous carbon component of these films can be expected to improve fracture toughness by limiting crack nucleation and by reducing the stress near existing cracks. Therefore, the excellent interfacial adhesion observed for these films (in comparison to crystalline diamond films) may be attributed to a reduction of residual film stress along with an increase in interfacial toughness.

The SEM analysis revealed circumferential microcracking surrounding some of the indentations. Figure 4 shows SEM micrographs surrounding the indents produced from 30- to 150-kg indents. Indents at 30, 60, 100,

TABLE I. Average and standard deviation of several characterization parameters described in this work.

	Mean	Standard deviation
Film thickness (μm)	4.0	0.4
rms Surface roughness (nm)	14	1
% Crystallinity	48	5
Residual stress (GPa)	5.5	0.6
% Strain for 30-kg load	0.7	0.1
% Strain for 60-kg load	1.1	0.1
% Strain for 100-kg load	1.9	0.1
% Strain for 150-kg load	2.8	0.2

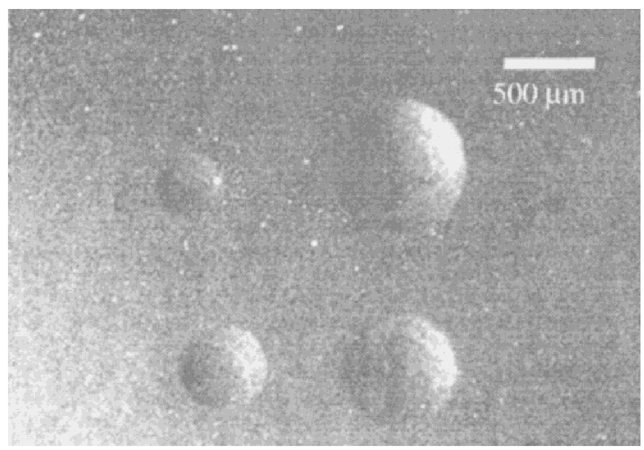

FIG. 1. Optical micrograph showing a set of four indentations on a diamond-coated titanium alloy. The indentation loads (counterclockwise from upper left) are 30, 60, 100, and 150 kg. No film delamination was observed.

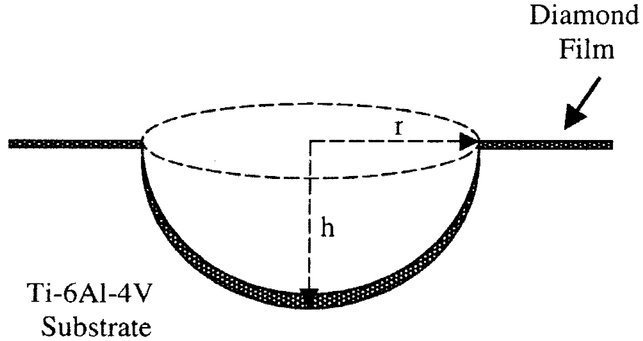

FIG. 2. Schematic of indentation produced on diamond-coated Ti–6Al–4V showing the parameters used to calculate film strain.

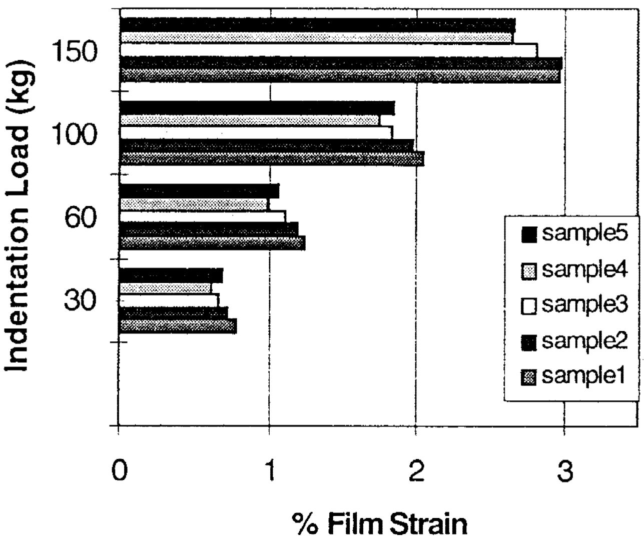

FIG. 3. Film strain variation with indent load measured from indentation surface areas and their corresponding projected surface areas. The average strain at 100-kg load indents (1.9 ± 0.1%) provides an upper limit of the strain to cause microcracking for these films.

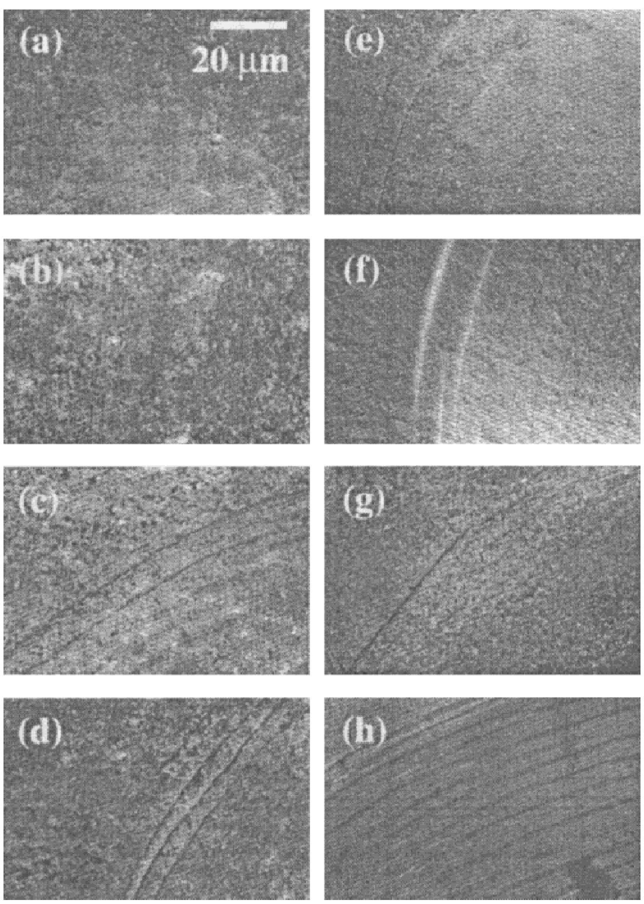

FIG. 4. SEM micrographs surrounding the indents produced from 30-kg to 150-kg indents. Indents at 30, 60, 100, and 150 kg from one sample are shown in (a–d) and indents from 150 kg loads from the remaining four samples are shown in (e–h).

and 150 kg from one sample are shown in Figs. 4(a)–4(d) and indents from 150-kg loads from the remaining four samples are shown in Figs. 4(e)–4(h). Despite the similar processing conditions, there was significant variation from sample to sample of the indentation load at which cracking became observable. For example, although microcracking was never observed for films indented at 30 kg (0.7% strain), some films showed microcracks at 60 kg (1.1% strain) whereas others did not show cracking until 150-kg (2.8% strain) loads were used. The number of circumferential cracks produced at a given load showed some variation from sample to sample as can be seen from Figs. 4(e)–4(h). When a 75-μm perpendicular test line was drawn from the outermost crack visible on 1000× micrographs toward the center of 150-kg indents of each of the samples, between three and twelve cracks were counted. The number of cracks observed did not appear to correlate with the small variations from sample to sample in film thickness, film strain, or percent crystallinity. Although the standard deviation of these parameters for all five films is small, an even tighter control of the CVD processing conditions may result in more consistent microcracking behavior between films. Despite the variation in film cracking when comparing the five films, the excellent interfacial adhesion and minimal cracking are encouraging.

Because no cracking was observed for any of the 30-kg indents, the average film strain at this load (0.7 ± 0.1%) represents a lower limit of strain to cause microcracking. In addition, because some of the films did not show microcracking until 150-kg loads were used, the average film strain at 100-kg indents (1.9 ± 0.1%) provides an upper limite of the strain to cause microcracking. This value of strain is indicative of a particular ductile coating when compared to most ceramic materials. For example, for a predominantly crystalline diamond film in which almost no plastic flow is expected to occur before fracture or delamination, a strain of 1.9% would result in a biaxial stress in the film of

$$\begin{aligned} \sigma &= \epsilon_f \{E/(1-\nu)\} \\ &= 0.019\{1050\ \text{GPa}/(1-0.07)\} \\ &= 22\ \text{GPa} \quad . \end{aligned} \tag{4}$$

It is likely that this stress in a diamond film that is predominantly crystalline is too high to prevent fracture or delamination.[7]

Clearly, the nanostructured diamond films in this study can undergo significant plastic deformation without hard elastic to brittle fracture occurring. Similar hard and tough nanocrystalline/amorphous composite coatings have been produced in other systems such as those involving titanium carbide particles in an amorphous carbon matrix.[8] The observed ductility of our coatings is not expected to be a result of dislocation motion because the grain size (10–15 nm) is too small to act as a sufficient source of dislocation activity. Instead, nanometer-size cracks are likely to develop along grain boundaries. These nanocracks are not catastrophic, but terminate within the surrounding amorphous matrix, which acts to relax incoherence stress and distribute the localized load over larger volumes.[9] The fact that film cracking was not always observed at the SEM magnifications used in this study (even for some indentation loads as high as 100 kg) is supported by previous reports that such nanocracks require higher magnifications.[9]

In conclusion, the high hardness, low surface roughness, excellent interfacial adhesion, and resiliency of these coatings makes them prime candidates for tribological applications. Future studies involving transmission electron microscopy will be used to study nanocrack formation at various indentation loads.

ACKNOWLEDGMENT

This research is supported by National Science Foundation—Research Experiences for Undergraduates—site award under DMR-9619405.

REFERENCES

1. D.M. Gruen, S. Liu, A.R. Krauss, J. Luo, and X. Pan, Appl. Phys. Lett. **64,** 1502 (1994).
2. D. Zhou, T.G. McCauley, L.C. Qin, A.R. Krauss, and D.M. Gruen, J. Appl. Phys. **83,** 540 (1998).
3. D. Zhou, A.R. Krauss, L.C. Qin, T.G. McCauley, D.M. Gruen, T.D. Corrigan, R.P.H. Chang, and H. Gnaser, J. Appl. Phys. **82,** 4546 (1997).
4. S.A. Catledge and Y.K. Vohra, J. Appl. Phys. **84,** 6469 (1998).
5. S.A. Catledge and Y.K. Vohra, J. Appl. Phys. **86,** 698 (1999).
6. S.A. Catledge, W. Comer, and Y.K. Vohra, Appl. Phys. Lett. **73,** 181 (1998).
7. J.W. Ager and M.D. Drory, Phys. Rev. B **48,** 2601 (1993).
8. S. Veprek, J. Vac. Sci. Technol., A **17,** 2401 (1999).
9. A.A. Voevodin and J.S. Zabinski, J. Mater. Sci. **33,** 319 (1998).