



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Surface and Coatings Technology 174–175 (2003) 402–407

**SURFACE
& COATINGS
TECHNOLOGY**www.elsevier.com/locate/surfcoat

Pulsed laser deposition of diamond-like carbon coatings for industrial tribological applications

J.M. Lackner^{a,b,c,*}, C. Stotter^{a,b}, W. Waldhauser^b, R. Ebner^{a,b}, W. Lenz^b, M. Beutl^d^aMaterials Center Leoben, Franz-Josef-Strasse 13, Leoben A-8700, Austria^bJOANNEUM RESEARCH, Laser Center Leoben, Leobner-Strasse 94, Niklasdorf A-8712, Austria^cInstitute of Physical Metallurgy and Materials Testing, University of Leoben, Franz-Josef-Strasse 18, Leoben A-8700, Austria^dJOANNEUM RESEARCH, Institute for Nanostructured Materials and Photonics, Franz-Pichler-Strasse 30, Weiz A-8160, Austria

Abstract

The aim of the present work is the investigation of the structural, mechanical and tribological properties of low-wear diamond-like carbon (DLC) coatings for industrial applications. Amorphous hydrogen-free (a-C) and hydrogenated (a-C:H) DLC coatings were coated onto various steel substrates (AISI 1045H, B7, H13, D2, M2) with hardness levels varying from 28 to 66 HRC, by employing the pulsed laser deposition (PLD) method. Therefore, graphite targets were ablated with the 1064 nm wavelength of an Nd:YAG laser in argon and C₂H₂ atmospheres. The high mean laser power of the applied PLD equipment guarantees deposition rates competitive to other physical vapour deposition (PVD) techniques. Because of the specific process conditions and the use of pure titanium adhesive interface layers, coatings with high adhesion to the substrates were produced at room temperature. The investigations of the coatings by means of light and scanning electron microscopy reveals the high surface quality and extremely dense coating structures. XRD measurements indicated the amorphous structure of the coatings. The nature of the chemical bonding was examined by XPS, indicating different amounts of sp³ carbon bonds. Pin-on-disc tests against 100Cr6 ball-bearing steel balls as counterparts show an excellent wear resistance of a-C and a-C:H DLC coatings on all different steel substrates. These results, demonstrated the applicability of PLD–DLC coatings for wear protection of high precision components in the field of tools and mechanical components.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Thin films; Coating technology; Diamond-like carbon; Pulsed laser deposition; Wear; Wear mechanisms; Transfer layer; Abrasion

1. Introduction

During the previous years, coatings of amorphous diamond-like carbon (DLC) have been one of the exciting research topics in materials science and structural engineering, all over the world. These coatings have very attractive tribological properties such as low friction, high hardness, chemical inertness and high surface quality [1]. In contrast to most of the other wear resistant hard coatings, DLC coatings not only exhibits low friction coefficients and low film wear rates, but can also protect the opposite rubbing surface from significant wear [2]. This unique feature makes the DLC coatings more attractive and promising in applications to improve the tribological performance of mechanical

components which are in sliding contact, e.g. in structural engineering or in tooling applications.

These beneficial properties of DLC are due to the mixture of tetrahedral (sp³) and trigonal (sp²) bonding constituents of carbon in the coating [1]. Furthermore, the mechanical properties (e.g. hardness, Young's modulus, adhesion to the substrate, internal stresses) as well as important electronic properties (e.g. optical gap, photoluminescence, conduction behaviour) could be tailored, to a certain extent by varying the sp³/sp² bonding ratio [1]. Deposition of DLC films can be accomplished at low substrate temperatures and at high deposition rates, by utilizing a wide range of PA-CVD and PVD methods, including pulsed laser deposition (PLD) [1]. In the latter technique, a pulsed laser beam is focused onto a target to evaporate its surface. The vaporised material—consisting of atoms, ions and atomic clusters—is then deposited onto the substrate, which is mounted opposite to the target, in the vacuum chamber.

*Corresponding author. Tel.: +43-3842-402-730; fax: +43-3842-402-737.

E-mail address: j.lackner@unileoben.ac.at (J.M. Lackner).

Table 1
Hardness and surface roughness of various substrate materials

Substrate, AISI (DIN)	Hardness (HRC)	Roughness R_a (nm)
1045H (Ck 45)	28.9±0.5	4.01
B7 (42 CrMo 4)	50.9±0.5	4.24
H13 (X40 CrMoV 5 1)	52.6±0.5	4.43
D2 (X155 CrVMo 12 1)	59.8±0.5	7.19
M2 (HS 6-5-2)	65.6±0.5	5.69

The most important advantage of this method is the possibility of varying the sp^3/sp^2 ratio in the DLC coatings, because of the high kinetic energy of the vaporised material [3]. Furthermore, a deposition of both hydrogenated (a-C:H) and hydrogen-free (a-C) DLC coatings too, is possible at deposition rates which are comparable to other CVD and PVD processes [4,5].

Despite the superior tribological properties of PLD–DLC films, as demonstrated by several authors in the recent years [4–6], a breakthrough in the industrial applications for tools and structural components would not be achieved. The lack of large facilities in PLD coatings might be one of the major causes. In addition, the knowledge about the friction and wear data for PLD–DLC films, deposited onto steels of different hardness at common humidities (50–60%) is very limited so far. To close this gap in the present work, five common steels of mechanical components and tools were coated with a-C and a-C:H DLC films, in order to investigate the mechanical and tribological behaviours of industrially applicable coatings.

2. Experimental

2.1. Film deposition

Electro-graphite targets (99.5% carbon, impurities of vanadium, titanium, hydrogen and oxygen) were used for the ablation experiments using a pulsed Nd:YAG laser, which provides a beam of 1064 nm wavelength, 1 J pulse energy and 10 ns pulse duration at a repetition rate of 10 Hz [7,8]. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (approx. 25 °C) in argon or C_2H_2 atmospheres onto quenched and tempered steel substrates (AISI 1045H, B7, H13, D2, M2), of different hardness with mirror-polished surfaces (Table 1). Deposition rates between 15 and 35 nm/min have been reached for both a-C and a-C:H coatings, deposited in Ar, respectively; C_2H_2 atmospheres, which are partially, extremely higher as compared with DLC deposition with most of the other well-known methods of PVD and CVD. Prior to film deposition, the substrates were cleaned ultrasonically in pure acetone and ethanol. To increase the adhesion to the substrate titanium adhesive interface layers were deposited prior to the carbon deposition.

2.2. Film characterisation

The surface quality, growth structures and wear scars of the coatings were inspected with a light and a scanning electron microscope (Cambridge Instruments Stereoscan 360). The latter was equipped with energy and a wavelength dispersive analyser (EDS and WDS), for chemical analysis.

X-Ray photoelectron spectroscopy (XPS) was employed to investigate the chemical bonding in the coatings, using an Omicron Multiprobe system with a monochromised $AlK\alpha$ (1486.6 eV) X-ray beam and an EA 125 energy analyser. The spectrometer was operated in fixed analyser energy transmission mode (FAT), at a base pressure of 4×10^{-9} Pa. The resolution of the chosen set-up is better than 0.6 eV and the detection sensitivity is approximately 1 vol.%. For cleaning the samples, an Omicron 'ISE 10' sputter gun using Ar^+ ions was applied.

The hardnesses and Young's moduli of the films have been determined by nano-indentation with a Berkovich indenter. The applied maximum load was approximately 10 mN and the loading rates were approximately 20 nm s^{-1} for all measurements. The indentation depth (~ 125 nm) and the film thickness (~ 600 nm) were kept constant to prevent substrate influences and indentation-size effects.

The dry sliding friction of the DLC films at room temperature (25 °C) was evaluated using, a CSEM Instruments high-temperature pin-on-disc tribometer with 6 mm 100Cr6 bearing steel balls as counterparts. All experiments were carried out on the as-deposited, ultrasonically cleaned coatings surfaces. The applied load was 2 and 10 N at a sliding speed of 0.1 m s^{-1} . Optical profilometry (Veeco NT-1000) was used to inspect wear tracks for analysing wear mechanisms and wear coefficients, as well as for the characterisation of surface roughness.

3. Results and discussion

3.1. Physical and chemical properties of DLC films

SEM investigations of fracture sections of all coatings, revealed dense coating structures and very smooth surfaces with only a few defects (e.g. larger particulates ablated from the target). The corresponding roughnesses are given in Table 2. The slightly higher roughness of the a-C:H coatings might be caused by the higher deposition rates, and lower energies of the deposited species in C_2H_2 atmospheres, as argued by Ebihara et al. [9]. The reason for this phenomenon is the superposition of the high-energetic species ablated from the graphite target, and the relatively low-energetic species delivered by dissociation of the process gas. XRD

investigations of 4 μm thick coatings on molybdenum substrates indicated an amorphous structure.

XPS investigations of the C1s peak lead to a sp^3 carbon bond content of approximately 36% for a:C coatings and 23% for a-C:H films. These values were evaluated by fitting the C1s peak with the two main components, diamond represented by sp^3 bondings (peak at 285.2 eV) and graphite represented by sp^2 bondings (peak at 284.4 eV), and by calculating the areal fractions under the peaks [10]. Furthermore, small contents of C–O bondings were detected. The contribution of the background was approximated by the Shirley method. The XPS spectra of both films, and the deconvolution in diamond and graphite correspondent contents are shown in Fig. 1. The relatively low sp^3 contents of the coatings are in agreement with Voevodin's observation [4], of the growth of mainly graphitic films that are produced by PLD of carbon, employing 1064 nm Nd:YAG laser radiation at laser pulse power densities, lower than $10^{11} \text{ W cm}^{-2}$.

Quantitative information about the adhesion of the DLC coatings to the M2 steel substrate was supplied by Rockwell indentations [11]. For both types of coatings with a thickness of approximately 600 nm on substrate materials, with hardness higher than 54 HRC (D2, M2), an adhesive strength class HF 2–3 was found, which is connected to some small break-out areas around the indentation, and some short cracks. Nano-indentations revealed a significant lower hardness and Young's modulus of the a-C:H coatings (Table 2), caused by the lower sp^3 content [4].

3.2. Tribological properties of the films

3.2.1. Friction coefficient evolution and wear mechanisms

The coefficient of friction, the wear mechanism and the wear rate of the PLD–DLC coatings were investigated in dependence on the chemical composition of the films, and the substrate hardness at common industrial conditions (room temperature, relatively high ambient relative humidities of approximately 60%). Examples of frictional curves of a-C and a-C:H coatings on M2 steel substrates, which are representative for all substrates, are shown in Fig. 2.

During the short run-in (sliding distance of approx. 20 m), the frictional coefficient fluctuated in the range of 0.10–0.25, which might be due to the initial roughness of the two surfaces in contact, is followed by

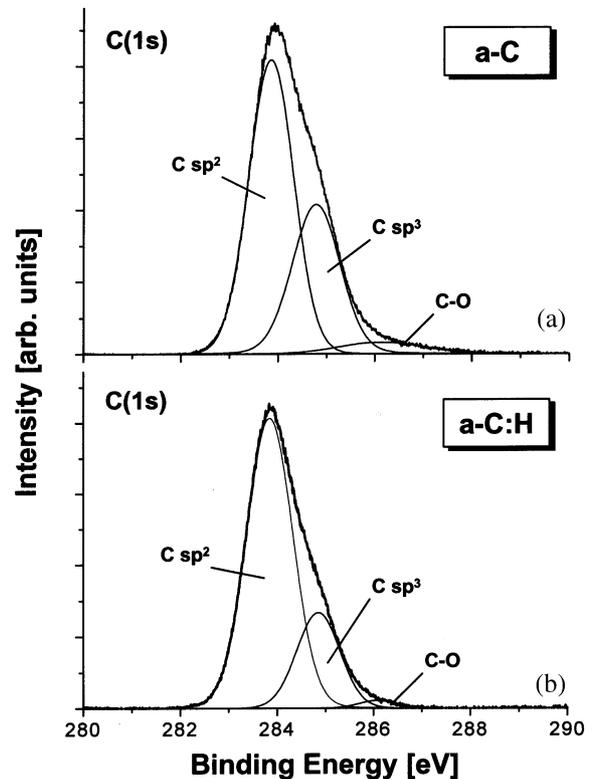


Fig. 1. XPS spectra of the C1s peak of (a) hydrogen-free (a-C) and (b) hydrogen-containing (a-C:H) DLC film. For the deconvolution of the measured cumulative peak, the sp^2 , sp^3 and C–O peaks, each being a mixture of a Gaussian and Lorentzian peak, have been applied.

asperity cracking and formation of wear debris as argued by Holmberg et al. [2]. After the run-in phase, the frictional coefficient remains constant, but it is strongly dependent on the ambient humidity. A reduction of the humidity from 60% down to 40% leads to a significant drop of the frictional coefficient from approximately 0.20 to approximately 0.05–0.07, which is in accordance with the observation of various authors (e.g. [12–14]). The wear mechanisms of the coatings are strongly dependent on the substrate hardness (see chapter 3.2.3). At the surface of the counterpart (100Cr6 steel ball) abrasive wear and the formation of nearly pure carbon wear debris, with high adhesion to the steel ball can be observed (Fig. 3). Comparable formations of wear-protective graphitic layers, containing mainly transfer materials from the coatings, have been widely reported in the literature [15,16]. The total sliding distance up to the end of the wear lifetime of the coating is strongly

Table 2
Properties of the DLC films deposited

Types of coating	Process gas (deposition)	Roughness R_a (nm) (on M2)	sp^3 content (%)	Hardness (GPa)	Young's modulus (GPa)
a-C	Argon	6.74	36	19.9 ± 0.6	190.0 ± 3.5
a-C:H	C_2H_2	8.35	23	6.6 ± 0.6	164.8 ± 2.1

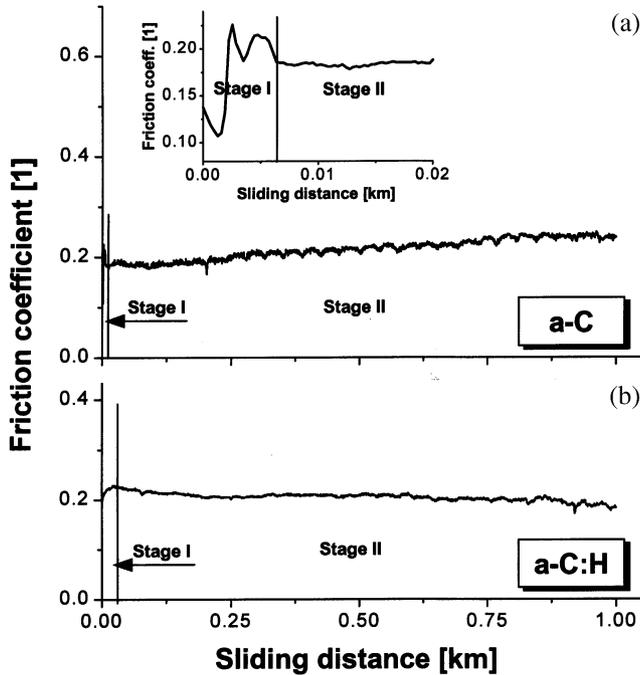


Fig. 2. Characteristics of the friction coefficient in dependency of the sliding distance in the pin-on-disc test (10 N, 0.1 m s⁻¹, 25 °C, 60% humidity) for (a) a-C and (b) a-C:H DLC films on M2 steel substrates (65.6 HRC). The detail in (a) shows the run-in phase of the a-C film.

dependent on the combination of applied load and substrate hardness. This state is characterised by a fast increase of the frictional coefficients to approximately

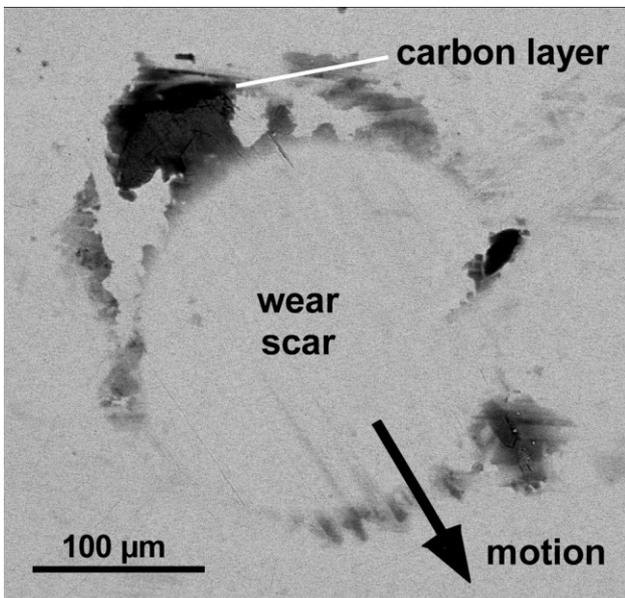


Fig. 3. SEM micrograph of the wear scar and the carbon transfer layer of a 100Cr6 ball-bearing steel counterpart after 1000 m sliding on a a-C film (10 N, 0.1 m s⁻¹, 25 °C, 60% humidity), deposited on H13 steel substrate.

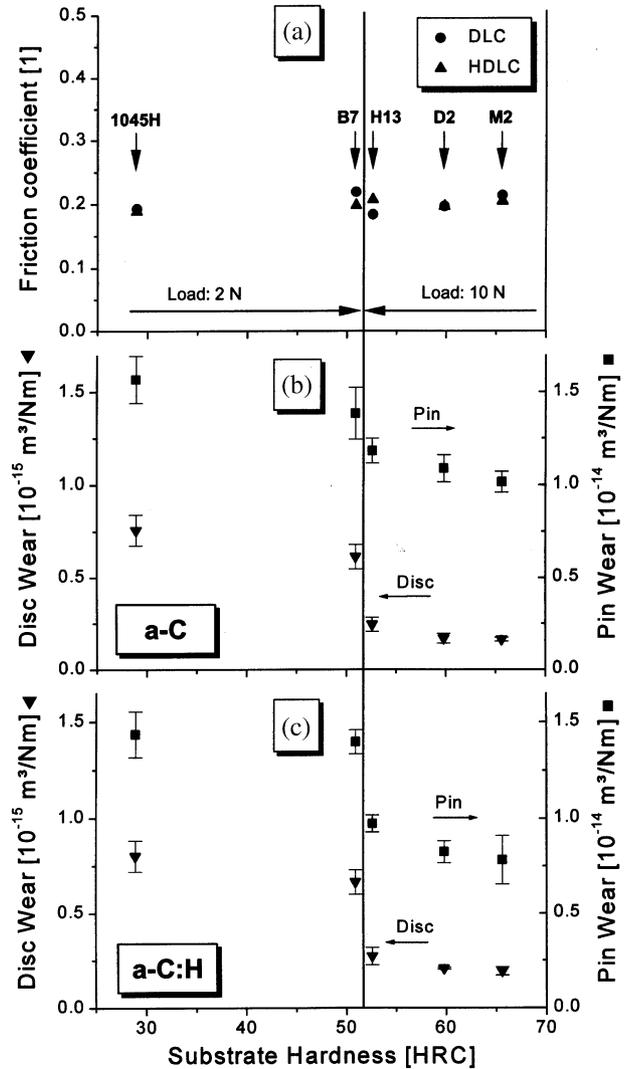


Fig. 4. Influence of substrate hardness on the (a) frictional coefficient, on the (b) wear of a-C films and 100Cr6 counterparts and on the (c) wear of a-C:H films and 100Cr6 counterparts.

0.7, representing the characteristic value of steel/steel contact.

3.2.2. Effect of sp^2/sp^3 ratio and hydrogen content to friction and wear

Pin-on-disc tests performed at the higher humidity of 60%, reveals no significant influence of the sp^2/sp^3 ratio and hydrogen content on the friction and wear behaviour (see Fig. 4a), in accordance to Holmberg [2], although significant differences in the hardness and the Young's modulus were given. On the other hand, the film wear rates on the substrates of different hardnesses investigated, are strongly dependent on the sp^2/sp^3 ratio. The sp^3 richer a-C coatings of higher hardness proved to be more wear resistant compared with sp^2 richer, softer a-C:H coatings (Fig. 4b and c). In contrast, the counterparts sliding against a-C coatings, suffered from

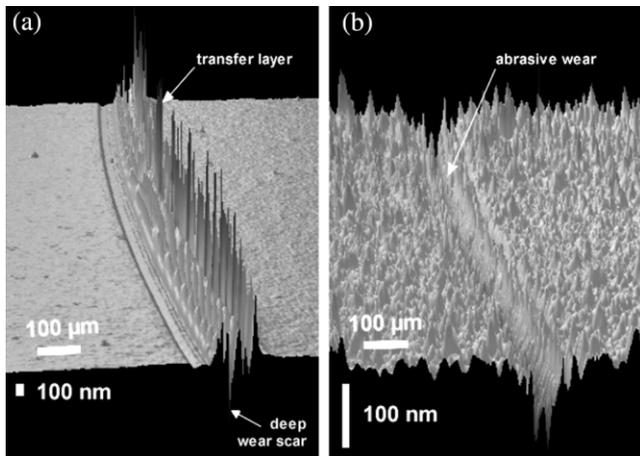


Fig. 5. Three-dimensional views from optical profilometry investigations of the wear tracks of a-C:H films, deposited onto a (a) H13 and (b) M2 steel substrate after the run-in period (50 m, 10 N, 0.1 m s⁻¹, 25 °C, 60% humidity), indicating different wear mechanisms: (a) centre cracks leading to transfer layers, (b) pure abrasive wear without cracks in the film.

more severe wear than compared to counterparts sliding against a-C:H coatings. These phenomena were found for CVD–DLC coatings too [17], and can be attributed to the higher hardness due to the higher sp³ content of the a-C coatings.

3.2.3. Effect of substrate hardness on friction and wear

Comparing the frictional coefficients after the run-in of a-C:H and a-C films (Fig. 4a), values in the range of 0.18–0.21 can be observed in the regime of high humidity (60%), which is independent of the substrate hardness. This behaviour is in accordance with the investigations of CVD–DLC coatings deposited on aluminium substrates of different hardness [18].

In contrast, wear is significantly influenced by the substrate hardness. High plastic deformation of the substrates with lower hardness (1045H, B7, H13) occurs during testing, presenting a maximum value at the centre of the wear track [19]. Optical profilometry observations indicated, pushed-out material at the borders of the track too (Fig. 5a). The brittle coating cannot follow this deformation leading to crack nucleation and propagation in the highest deformed areas. Due to high adhesion to the substrate, only very small parts of the coatings delaminate and forms, wear debris (see SEM micrograph in Fig. 6a). Abrasive wear as well as the formation of transfer layers (see, Fig. 5a), after debris accumulation in the wear track, can be initiated by losing this debris. The latter may be caused by the high chemical reactivity of the carbon, and the metallic titanium of the adhesive interface layer, combined with the high temperatures, occurring during the frictional contact at local ‘hot spots’ [20]. No formation of a transfer layer was found during pin-on-disc tests of DLC coatings without adhesive

titanium interfaces under the same testing parameters. Furthermore, WDS examinations of the transfer layers showed high contents of carbon, iron, oxygen (from the atmosphere) and titanium.

The threshold for the crack nucleation, leading to the formation of transfer layer was found between substrate hardness levels in the range of 53 and 59 HRC for 10 N, applied normal load at sliding speeds of 0.1 m s⁻¹ for both a-C and a-C:H coatings. If the plastic deformation of the substrate is too high, which was found e.g. for 1045H and B9 steel substrates at a load of 10 N, rapid crack nucleation and propagation occurs not only at the centre, but also at the borders of the worn area. Due to large delaminated areas, the frictional coefficient rapidly rises to approximately 0.7 (steel/steel contact). The wear lifetime in these cases was very low (approx. 10 m sliding distance). To prevent cracking at the borders of the worn area, the load was reduced to 2 N. This again leads to the formation of a transfer layer. If the substrate hardness exceeded the threshold, for preventing the cracking of films, only when abrasive wear of the films occurred. This was found in the pin-on-disc tests performed on the films deposited onto D2 and M2 steel substrates (Fig. 6b). Furthermore, very low depths of the wear track (Fig. 5b) were observed.

Comparing the wear rates of both a-C and a-C:H coatings, deposited onto substrates of different hardnesses were investigated, and a slight tendency to lower the film wear could be found at higher substrate hardnesses (Fig. 4b,c). For these considerations, only the lost volume of the films was taken into account, and not the volume of the transfer layers. In addition, the wear rate

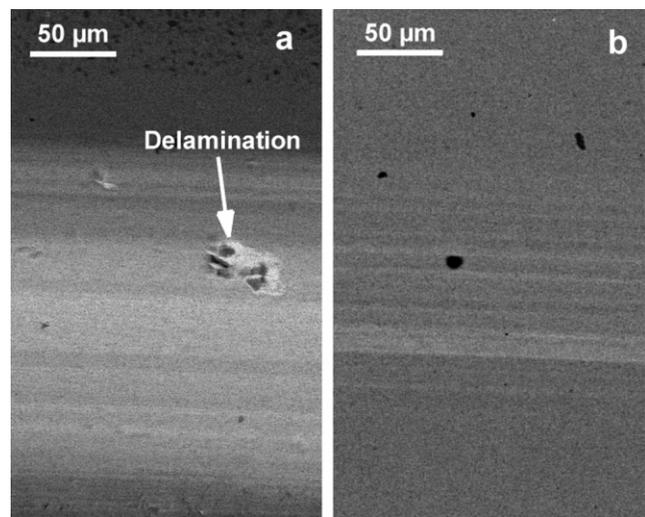


Fig. 6. SEM micrographs of the wear tracks of a-C:H films, deposited onto a (a) H13 and (b) M2 steel substrate after the run-in period (50 m, 10 N, 0.1 m s⁻¹, 25 °C, 60% humidity), indicating different wear mechanisms: (a) delamination of the coating leading to transfer layers, (b) pure abrasive wear without cracks in the film.

of the 100Cr6 ball follows the same tendency; in accordance to reports from Ronkainen [17], as well as the higher wear rates for the lower loads. The latter phenomenon is due to the load dependency of wear tests, and is strongly related to the Holm wear relationship [2].

4. Conclusion

Hydrogen-free (a-C) and hydrogenated (a-C:H) amorphous diamond-like carbon (DLC) coatings were deposited, with a pulsed laser deposition (PLD) system by ablation of electro-graphite targets in argon and C₂H₂ atmospheres. The very smooth and dense coatings showed, good adhesion to the steel substrates of various hardnesses ranging from 28 to 66 HRC. Tribological investigations (pin-on-disk tests) were carried out at common ambient conditions (60% humidity and 25 °C), leading to frictional coefficients of approximately 0.2, for both a-C and a-C:H coatings on all substrate materials. The wear mechanisms are strongly dependent on the hardness of the substrate. At low substrate hardness levels, a transfer layer occurs after delamination of film particles, due to high plastic deformation of the substrate under the friction load, whereas at hardness levels above 53 to 59 HRC for 10 N, load abrasions were found to be the main wear mechanism. In general, a-C coatings showed lower wear rates than a-C:H coatings. In contrast, sliding on a-C:H coatings leads to lower wear of the counterpart. Summing up, the presented PLD–DLC coatings shows an excellent tribological properties for the industrial application in the fields of cutting and forming tools, bearings and medical implantations.

Acknowledgments

Financial support of this work by the Austrian Federal Ministry of Traffic, Innovation and Technology, the Austrian Industrial Research Promotion Fund (FFF), the Government of Styria, the Technologie Impulse Gesells-

chaft mbH in the frame of the Kplus Programme and the European Union is highly acknowledged. The authors are grateful to Dr T. Schöberl (Erich-Schmid Institute, Austrian Academy of Sciences, Leoben) for the nano-indentations and to M.H. Wong (The Hong Kong Polytechnic University, China) for preparing the coated samples at Laser Centre Leoben.

References

- [1] J. Robertson, *Mater. Sci. Eng. R* 37 (2002) 129.
- [2] K. Holmberg, A. Matthews, *Coatings Tribology*, Elsevier, Amsterdam, 1994.
- [3] D.B. Chrisey, G.K. Hubler, *Pulsed Laser Deposition of Thin Films*, Wiley, New York, 1994.
- [4] A.A. Voevodin, M.S. Donley, *Surf. Coat. Technol.* 82 (1996) 199.
- [5] A.A. Voevodin, M.S. Donley, J.S. Zabinski, *Surf. Coat. Technol.* 92 (1997) 42.
- [6] Q. Wei, A.K. Sharma, J. Sankar, J. Narayan, *Compos. B* 30 (1999) 675.
- [7] W. Lenz, *Laserunterstützte Beschichtungstechnologie*, Ph.D. Thesis, University of Leoben, Austria, 1997.
- [8] J.M. Lackner, W. Waldhauser, W. Lenz, R. Ebner, C. Suess, G. Jakopic, G. Leising, H. Hutter, *Surf. Coat. Technol.* 163–164 (2003) 300.
- [9] K. Ebihara, T. Namiya, *Diamond Rel. Mater.* 10 (2001) 900.
- [10] P. Merel, M. Tabbal, M. Chaker, *Appl. Surf. Sci.* 136 (1998) 105.
- [11] H. Jehn, G. Reiners, N. Siegel, *DIN-Fachbericht 39, Charakterisierung dünner Schichten*, Beuth, Berlin, 1993.
- [12] Y. Özmen, A. Tanaka, T. Sumiya, *Surf. Coat. Technol.* 133–134 (2000) 455.
- [13] E.-S. Yoon, H. Kong, K.-R. Lee, *Wear* 217 (1998) 262.
- [14] R. Gilmore, R. Hauert, *Surf. Coat. Technol.* 133–134 (2000) 437.
- [15] H. Ronkainen, J. Likonen, J. Koskinen, *Surf. Coat. Technol.* 79 (1996) 87.
- [16] R. Memming, H.J. Telle, P.E. Wierenga, *Thin Solid Films* 143 (1986) 31.
- [17] H. Ronkainen, J. Koskinen, J. Likonen, *Diamond Films 93 Conference, Albufeira, Portugal, 1993*, p. 30.
- [18] J. Jiang, R.D. Arnell, J. Tong, *Wear* 211 (1997) 254.
- [19] J. Jiang, R.D. Arnell, *Wear* 217 (1998) 190.
- [20] Y. Liu, A. Erdemir, E.I. Meletis, *Surf. Coat. Technol.* 82 (1996) 48.