STUDIES ON DEPOSITION, PROPERTIES AND APPLICATIONS OF TETRAHEDRAL AMORPHOUS CARBON FILMS

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ACADEMIC DISSERTATION

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ABSTRACT

Tetrahedral amorphous carbon (ta-C) is a very promising material for biomechanical and industrial applications because it is chemically inert, biocompatible and extremely hard. Our experiments show that with ta-C the wear resistance of hip implants can be improved by a factor of one million when compared with common commercial ones. The poor wear resistance limits the lifetime of currently available hip implants to 5-15 years, which is below the life expectancy of the average patient. The extreme physical properties of ta-C also make it suitable for various industrial applications. In our experiments with paper mill sensors and water jet cutters, ta-C coating on contact surfaces significantly reduced wear and accumulation of resin. Moreover, with ta-C it was possible to measure higher paper coating paste shear rates ($10^7$ 1/s) than with any other material used in paper paste viscometer nozzles.

These applications have become feasible because we have solved the problems related to the adhesion of ta-C. To overcome the adhesion problems due to the internal stress of ta-C, one needs good control over plasma energy. We have developed a new optical method to measure the plasma energy and a simple adhesion and quality evaluation method that tests the deposition process as a whole. These combined with the possibility to adjust the plasma energy allow us to deposit thick (>10 µm) ta-C coatings necessary for demanding industrial and biomedical applications.
LIST OF PUBLICATIONS

This thesis consists of a summary and the articles listed below. In the summary the articles are referred to by the following Roman numerals (I-V):


Due to the diverse nature of the research, all of the articles except Article II have been produced as a group effort by the Helsinki University Diamond Group. The author’s main contribution has been participating in the development, maintenance and operation of the deposition system (Articles I-V), in sample preparation (Article I), in the construction of the optical analysis system (Article IV) and in the surface analysis of the samples (Article V). Article V shows how the ideas of Article I can be implemented in practice to get feedback on the system. Article II provides a complete review of the group’s biomechanical research and outlines its principal field of research. As a group member, the author has actively participated in the groundwork and scientific activities enabling this research. The author has also had the principal responsibility for typing and formulating all of the articles.

The experimental part of this study was conducted mainly in the Accelerator Laboratory of the University of Helsinki. Part of the experiments in Article III were conducted at the Department of Applied Physics of the University of Kuopio, in the paper mills of United Paper Mills Ltd. and in facilities provided by ACA Systems Ltd. The group is part of the Medical, Dental and Veterinary Biomaterial Research Group (BRG), which has been recognized as a National Group of Excellence by the Academy of Finland since the beginning of 1999.
1. INTRODUCTION

The first deposition method for amorphous diamond-like carbon (DLC) material was published in 1971 [1]. In their study, Aisenberg and Chabot used a direct ion beam to grow the films. To improve deposition speed, Aksenov et al. developed the plasma arc discharge method at the end of the 1970s [2]. It was not until some time later that the value of these innovations was understood. General interest in diamond-like coatings grew at the end of the 1980s, and tetrahedral amorphous carbon (ta-C) became an important field of research at the beginning of the 1990s [3].

Tetrahedral amorphous carbon has been studied at the University of Helsinki since the mid-1980s by the Helsinki University Diamond Group led by Professor Asko Anttila. He has been the driving force behind our research and his innovations have guaranteed the scientific success of the group. For the last ten years, our focus has been on improving the biocompatibility and wear resistance of medical implants. We have also developed protective coatings for the sensors and viscosimeters of the paper industry.

To harness the tribological properties of ta-C, we had to learn how to produce and control the highly energetic arc discharge plasmas necessary in the deposition process. For this purpose, we developed the filtered pulsed arc discharge deposition system (FPADDS) unique in the world (Figs 1-4) [4, Article I]. This system enables deposition of high-quality ta-C films on an industrial scale.

We have also adapted FPADDS to deposit novel diamond-like carbon-polymer–hybrid (DLC-p-h) coatings with striking non-stick properties combined with...
Figure 2. Electronic set-up of Filtered Pulsed Arc Discharge Deposition System. Breaker and ignition gaps define the threshold voltage of the ignition discharge. If the breaker gap is increased, the ignition voltage is higher and the ignition discharge stronger. Generated pre-plasma short-circuits the cathode and anode, igniting the main discharge. The arc runs as long as the energy stored in the RCL-circuit can maintain the discharge. The pulse form can be adjusted by changing the resistor (R). Power supplies charge capacitors continuously. Charging currents determine the ignition repetition rate and the charge of the main capacitors when the arc is ignited.

high hardness [5,6]. This new anti-soiling material type was developed in our laboratory and is the latest addition to the materials that can be deposited with arc discharge methods. Due to our long-term research, the Academy of Finland awarded us the status of a National Group of Excellence as part of the Medical, Dental and Veterinary Biomaterial Research Group (BRG) at the end of 1998.

Article I describes for the first time anywhere how thick, high-quality ta-C films can be deposited on almost any surface without adhesion problems. Article II summarises the group’s biomechanical research prior to the date of publication, whereas Article III illustrates how ta-C can be used as a protective coating for applications in the paper industry. Article IV shows how an optical spectrometer and Doppler shift can be used to determine the plasma energy. Moreover, contrary to earlier results [7-12], this study demonstrates that arc discharge plasmas can contain significant amounts of multiply charged ions. Article V presents a simple but reliable adhesion and quality evaluation method that tests the deposition process as a whole.

2. CARBON PLASMA AND TETRAHEDRAL AMORPHOUS CARBON

When carbon ions having a suitable energy (~80 eV [13]) collide with a surface, they form an amorphous network connected with sp³ diamond bonds. The sp³ bonding fraction measured with electron energy loss spectroscopy (EELS) is >85% for high-quality tetrahedral amorphous carbon and 100% for natural diamond. The remaining fractions are sp¹ and sp² hybridised carbon and graphite bondings [3].

Despite being amorphous, this material has many characteristics comparable with those of natural diamond, i.e. it is very hard, chemically inert, transparent and electrically insulating. It is therefore sometimes referred to as amorphous diamond (AD), although some authors find this expression contradictory [3] (see also Nomenclature, page 25). A general name for methods in which ions, atoms or clusters colliding with the substrate form the coating is physical vapour deposition (PVD).

Artificial diamond coatings can also be deposited with chemical vapour deposition (CVD) methods. The resulting films are usually polycrystalline and
The most straightforward PVD approach is the use of a suitable particle accelerator. With these isotope separators, the mass and energy resolutions are precise, and the quality of the films can be defined in a very controlled manner. Unfortunately, because the carbon ion yield and thus the beam current and deposition speed are very low in these mass-separated ion beam (MSIB) systems, they are best suited for basic research purposes. However, there are some niche applications, such as protecting computer hard disk heads, in which this approach can be industrially viable.

The deposition speed can be increased by a factor of one thousand when a suitable arc discharge unit is used. An electric discharge between the cathode and the anode transforms part of the cathode’s graphite into a gas of ionised carbon atoms, carbon plasma. Unlike in normal plasmas, the charged particles are not distributed evenly and the plasma plume does not appear electrically neutral. The high voltage between the cathode and the anode accelerates this non-equilibrium plasma towards the ring-shaped anode in such a way that part of the plasma flies through the anode. The plasma is usually confined and steered with a magnetic field. This plasma accelerator type, sometimes referred to as an end window plasma source, was presented for the first time by Maslov et al. [15]. No consensus exists on the exact acceleration mechanism, but it is usually ascribed to ion pressure, electron-ion friction and uneven charge distribution in the plasma [16].
Arc discharge can be continuous, but according to our experiences, plasma ion energy control is better when the arc discharge is pulsed. Furthermore, the mechanical and electrical construction of a pulsed system is simpler.

Arc discharge is a violent process comparable with a small lightning. All of the carbon emanating from the cathode is not ionised, but explosive arc discharge ejects microscopic graphite particles from the cathode. Due to the high melting point of the graphite, these macroparticles do not melt. Although they can be electrically charged, most of them are too heavy to be deflected by the magnetic field and they fly rectilinearly towards the anode and the vacuum chamber walls [17].

To prevent the macroparticles from reaching the target and deteriorating the film quality, the plasma is deflected from its original flight direction with a magnetic filter. Because the magnetic field can not deflect the graphite particles, they are filtered out. In our present system, the filter is a solenoid connected in series with the arc discharge stage, the main capacitors and the tuning resistor. By changing the geometry of the cathode, anode and solenoid and by adjusting the electric parameters, one can change the plasma energy and the filtering efficiency [17].

Normally, the deflection is roughly 90°, but the solenoid bending can be as high as 360° [18] or the solenoid can have an s-bend shape [19,20]. However, due to the multiple scattering, invariably some of the macroparticles reach the sample. By using a hydrocarbon gas as the carbon source, one can avoid the macroparticle formation, but the resulting films contain significant amounts of hydrogen [21,22].

The general name for the systems combining an arc source with a magnetic filter is filtered cathodic vacuum arc (FCVA). Another approach to decrease the number of macroparticles is the use of an anodic arc [23] but there is no data available in the literature if high-energy ions, necessary for high adhesion, can be produced in a controlled manner with this system.

3. ADHESION OF ta-C

Earlier, the main problem of PVD methods was the high internal stress of the film, which destroyed the coating and even the substrate [4]. This problem limited the maximum thickness of high-quality ta-C films to ~500 nm and prevented their use in most mechanical applications because films this thin were not sufficiently strong to protect the substrate. Under a heavy load, a thick ta-C film prevents the substrate from deforming, analogous to thick ice preventing a skater from falling into water. However, it is noteworthy that although the internal stress is usually disadvantageous it can also be used to determine the quality of the deposition process as described in Article V and in Section 3.1. Moreover, this effect can be used to form micromechanical structures such as field emission tips [24].

Article I describes how the adhesion problem can be avoided and how thick (>10 µm) coatings can be deposited. Free-standing films can also be prepared, although this technique requires further optimising. The basic demands are that the substrate is sufficiently soft (HV < 3 GPa) and that it forms carbides. If either of these requirements is not met one must use an intermediate layer with these properties and, naturally, with good adhesion to the substrate [25]. In addition, one must begin the deposition with high carbon ion energies (>200 eV) in order to form an ion mixing adhesion layer full of carbides [4,Article V]. The high-quality ta-C film can then be deposited on this very thin adhesion layer. A unit for producing high-energy plasma is
presented in Figure 4. Thus far, the coatings prepared have been ~200 µm at their thickest, but our experiments indicate that no upper limit exists for coating thickness.

The exact reason why the compressive force does not increase linearly and destroy the coating when the coating thickness is increased is still somewhat unclear. It is assumed that the soft substrate yields and releases the internal stress sufficiently to allow the ta-C film to grow thick enough to become self-supporting. The possibility to prepare free-standing ta-C films supports this hypothesis. Moreover, it seems that it is easier to prepare thick free-standing films whereas thin films tend to break apart when the substrate is dissolved. However, no theory completely explains this phenomenon.

Other techniques to cope with the adhesion problems related to the internal stress include the whisker composite [26] and thermal annealing methods [27,28], but these are both somewhat cumbersome and can not rival the method presented above. If the recently presented in situ ion beam annealing technique [29] can be applied also on ta-C, it could provide a new and practical way to control the internal stress. Nevertheless, the adhesion between the coating and the substrate has to be very good in the most demanding applications.

3.1. STRESS ANALYSIS

If a relatively thin cantilever with known mechanical properties is coated and the corresponding substrate bending measured, the internal stress $\sigma_F$ of the film can be calculated with Stoney equation, Eq. (1) [30], where $F_F$ is the film force, $d_F$ is the coating thickness, $w$ is the cantilever width, $\delta$ is the displacement of the free end of
the cantilever, \( E_S \) is the elastic modulus of the substrate, \( d_S \) is the thickness of the substrate, \( \ell \) is the cantilever length and \( \nu \) is the Poisson constant. The equation is valid if \( d_F \ll d_S \). In terms of substrate curvature, the stress can be rewritten as Equation (2), where \( R_0 \) and \( R \) are the substrate radii before and after deposition, respectively. The curvature information is simplest to obtain with a surface profiler (see Fig. 5).

\[
\sigma_F = \frac{F_F}{d_F \cdot w} = \frac{\delta \cdot E_S \cdot d_S^2}{3 \cdot \ell^2 \cdot (1 - \nu) \cdot d_F}
\]

\[
\sigma_F = \frac{E_S \cdot d_S^2}{6 \cdot (1 - \nu) \cdot d_F} \left( \frac{1}{R} - \frac{1}{R_0} \right)
\]

The literature value for the internal stress of good-quality ta-C is 8-11 GPa [4,31,32]. Because internal stress is dependent on the quality of the film, this phenomenon can be used for the coating process quality control (Article V). The maximum thickness of the highest quality ta-C coatings one can deposit on an industrial grade semiconductor silicon wafer is typically 500 nm. Thicker films can be deposited if the quality of the coating is decreased. In other words, the thickness where the coating starts to peel off indicates the quality of the coating – provided that the adhesion of the coating is known.

If the adhesion of the coating to the substrate is so good that the increasing compressive stress can not break the substrate–coating interface, the bonding between the substrate atoms must yield. This means that the interface adhesion exceeds the limit above which the bulk properties of the substrate dictate the overall adhesion of the coating. Beyond this point, further improvement of the interface adhesion is fruitless. Described in this manner, adhesion refers to the capacity of the coating-substrate system to resist breakdown.

Figure 5. 3D profilometer (KLA Tencor P15) located in the clean room facilities of the Physicum Building, Department of Physical Sciences, University of Helsinki.
The compressive stress of a ta-C coating can be sufficiently strong to break a silicon wafer surface when adhesion is good [4, Article V]. Therefore, if breaking of the silicon substrate occurs when the coating thickness is increased, it is evident that the adhesion of the coating to the substrate is stronger than the bondings of single crystal silicon and the preferred crack propagation direction is not along the interface, *i.e.* the interface adhesion is defined in terms of “better than bulk properties”. Thus, the overall adhesion is *as good as possible*, and the peeling thickness can be used to define the quality of the coating. The catastrophic nature of the failure in a single crystal silicon wafer guarantees that the compressive breakdown stress, and thus, the peeling thickness and the coating quality are well defined.

Using identical silicon wafers, the coating process can be tested as a whole. If the coating peels off without breaking the silicon substrate, the adhesion needs to be improved. If breaking occurs, the peeling thickness is inversely related to the quality of the film: lower peeling thickness means better quality. When both conditions are fulfilled – the coating peels off and breaks the substrate at the minimum thickness – the coating process is optimised. For each wafer type, the relation between peeling thickness and quality can be calibrated with other methods such as X-ray photoelectron spectroscopy (XPS). After this, the time required for one test is less than one hour, including the time for vacuum pumping. The material cost is the price of the silicon wafer. The test is simple, fast, reliable and inexpensive.

4. PLASMA DIAGNOSTICS

As indicated earlier, good control of plasma flow and energy is essential to obtain good adhesion and film quality. The coating process can be monitored as a whole with the stress analysis methods presented above or with such film quality analysis methods as nanoindentation, Doppler shift attenuation (DSA) [33], X-ray reflectometry (XRR) [34], XPS, EELS or nuclear magnetic resonance (NMR) [35]. One can also monitor the deposition process by measuring the oscillations of the RCL circuit. This together with film resistivity measurements and transparency comparisons are perhaps the fastest and simplest ways to monitor the deposition system. Nevertheless, all of these methods give indirect information on the properties of the plasma.

To obtain direct information on plasma energy, one can use electrostatic probes, such as Langmuir probe [36], or mass spectrometers [37]. One can also use pendulum and calorimetric methods [38] or a microbalance [39]. All of these methods can, however, be disturbed by the high electromagnetic fields, arcing and graphite particles generated in our system. Furthermore, extracting ions from rapidly changing plasma can be problematic. Our group therefore prefers to use methods in which the measurement equipment can be optically isolated from the plasma.

In the time-of-flight method [40, 41], part of the light emitted by the carbon atoms is collected with optical fibres when the plasma travels through the confining solenoid (Fig. 6). The light is led to detectors and amplified signals are registered with an oscilloscope. If an oscilloscope with suitable memory functions is used, several pulses can be averaged to give the average time-of-flight of the plasma between the fibre collimators. When the distance between the collimators is known, the average energy of the carbon plasma can be calculated (Fig. 6c). This approach is simple and straightforward but has some limitations.
Figure 6. Schematic representation of the time-of-flight method [40,41]. The oscillograms of the optical signals are presented at three consecutive points of time ($t_1 < t_2 < t_3$) during the arc discharge (a-c). The plasma energy can be calculated with the time-of-flight (tof) when the distance ($s$) between collimators is known (c). Typical arc discharge time is some tens of microseconds. The plasma-confining solenoid is omitted from the figure.

The relative accuracy of the time-of-flight method decreases when the plasma energy increases, and consequently, the plasma flight time between the detectors decreases. The distance between the detectors can not be increased infinitely because the length of the confining solenoid is limited. In addition, when the plasma transport path is increased, the signal gets weaker almost exponentially.

If the RCL-circuit oscillates, the voltage between the cathode and the anode is reversed and the plasma may travel backwards in the solenoid, disturbing the measurement. To prevent this, one must use pulse-rectifying equipment or a complicated pulse-forming network. With voltages and currents as high as those used in our system (up to 10 kV and 10 kA), both of these options are cumbersome and expensive.

4.1. DOPPLER SHIFT MEASUREMENTS

Because of the pulsed operation mode and high peak currents of our system, all measurement equipment must be immune to electromagnetic pulses (EMP). By using Doppler shift measurement [42,43] with a photographic optical spectrograph, no EMP protection is needed.

The principle of this measurement is presented in Figure 7. The light is collected with optical fibres and led to the spectrograph (Fig. 8). The light is collimated so that the fibres see only a small portion of the plasma travelling by the collimators. The collimators are placed at a known angle relative to the main axis of the plasma flow. The other end of the fibres is placed at the entrance slit of the spectrograph so that the light emanating from the fibres enters the spectrograph at the correct angle. The system is calibrated for each film with an external light source with known spectral lines. One can also use extra fibres to expose reference marks to assure the lateral alignment of the film (Figs 4 and 7).
\[ \frac{\Delta \lambda_1 \cdot c}{\lambda} = -v_x \cdot \sin \alpha + v_y \cdot \cos \alpha \]  
(3a)

\[ \frac{\Delta \lambda_2 \cdot c}{\lambda} = -v_x \cdot \sin \alpha - v_y \cdot \cos \alpha \]  
(3b)

The Doppler shifts produced by the velocity components \((v_x \text{ and } v_y)\), which are parallel to the probe plane, can be expressed as in Equation (3), where \(c\) is the speed of light, \(\alpha\) is the fibre angle relative to the direction of the plasma flow and \(\lambda\) is the unshifted wavelength. The corresponding wavelength shifts seen via fibres 1 and 2 are \(\Delta \lambda_1\) and \(\Delta \lambda_2\). Equations (3a) and (3b) can be used to derive the velocity components given in Equation (4):

\[ v_x = \frac{-c \cdot (\Delta \lambda_1 + \Delta \lambda_2)}{2 \cdot \lambda \cdot \sin \alpha} \]  
(4a)

\[ v_y = \frac{c \cdot (\Delta \lambda_1 - \Delta \lambda_2)}{2 \cdot \lambda \cdot \cos \alpha} \]  
(4b)

From these values, the combined energy of plasma related to axial and radial expansion can be calculated. However, the rotational velocity component of carbon ions is not taken into account, and therefore, the measurement underestimates the overall energy of plasma. This will be addressed in future measurements.

If it is assumed that \(v_x\) is negligible, Equation (3a) is reduced to Equation (5), and the energy of the plasma can be calculated simply from the relative shifts of a known spectral line. If the fibre configuration is symmetrical, the shift \(\Delta \lambda\) is half of the relative wavelength distance of the shifted lines. Absolute wavelength values are needed only for line recognition, and therefore, calibration of the system is simpler. In our measurements, the ion energies were so low that no relativistic corrections were needed.

\[ v_y = \frac{\Delta \lambda \cdot c}{\lambda \cdot \cos \alpha} \]  
(5)

Once the spectral lines of the carbon plasma have been recorded, the charge states associated with each line can be obtained from a suitable reference book [44]. Hence, the charge states present in the plasma can be obtained simply by determining which lines are exposed on the film. The relative charge-state fractions can be obtained by combining the line intensities on the film with relative line intensities of carbon, fibre wavelength transmittance and film wavelength sensitivity. The charge-state distribution obtained with a 4 kV arc discharge voltage is given in Figure 9.

The measurement range of our present system is 3500-5200 Å. The working range of the spectrograph is larger, but the fibres and the film limit the useful detection range. The lines of neutral carbon atoms were not detected, although their spectral lines are strong within the measurement range (see Table 1 in Article IV). Lines of residual gases (H, O, N) were also not detected, indicating that they disturb neither the Doppler shift nor the time-of-flight measurements.
Figure 7. Doppler shift method: (a) Schematic representation of the measurement set-up, where $\alpha$ is the fibre angle relative to the main axis of the plasma flow. Fibres 3 and 4 ($\alpha=90^\circ$) can be used for simultaneous time-of-flight measurement or as control and reference sources. Fibres 5 and 6 are lead to an external reference light source and are thus omitted from the figure. (b) Magnified photograph of the $\lambda_{C1}=4647.42$ Å line (left) and the superposition of $\lambda_{C2}=4650.25$ Å and $\lambda_{C3}=4651.47$ Å lines (right) measured simultaneously with $\alpha$ being 45° (fibres 1 and 2) and 90° (fibres 3 and 4). (c) Doppler shift of 4267.3 Å carbon line measured with $\alpha=45^\circ$ (fibres 1 and 3) and $\alpha=90^\circ$ (fibres 3 and 4). The helium reference lines $\lambda_{He1}=4259.4$ Å, $\lambda_{He2}=4266.5$ Å and $\lambda_{He3}=4272.2$ Å were exposed with fibres 5 and 6.

Earlier studies indicated that the single ionised state would be dominant for carbon [7-12]. In our measurements, the strongest population was three times ionised (Fig. 9). The difference in the results can be explained with the high arc discharge currents (7.5-10 kA) used in our system. Four times ionised carbon atoms were not detected in the measurements. However, their lines are very weak within the measurement range, and therefore, their existence can not be excluded. Actually, the ionisation energy of the 4+ state (64.5 eV) is close to that of the three times ionised state (47.9 eV) [44]. In addition, the shapes of the experimental charge-state distributions of carbon [Article IV] and other elements [7] suggest that the four times ionised population was present (see Fig. 9). The ionisation energies of the 5+ and 6+ states are significantly higher (392.1 eV and 490.0 eV, respectively), and thus, their existence is less likely.
Figure 8. Crossed dispersion spectrograph STE-1 (C73-1) with gratings for 220–450 nm and 450–900 nm measurements: (a) overview, (b) front panel with entrance slit and slit, shutter and grating selection controls, (c) back panel with the film cassette. The dimensions of the spectrograph are 1000 mm x 710 mm x 400 mm (lwh).

Figure 9. Experimental charge-state distributions of tantalum and zirconium (measured by Davis and Miller with 100 A arc current [7]) and carbon (this work, 7.5-10 kA [Article IV]). The distribution outlines are drawn to guide the eye. As can be seen, the distributions are normally continuous, and thus, it is reasonable to assume that also the carbon charge-state distribution would continue without a steep edge, although higher charge states were beyond the measurement range.
5. HIP IMPLANTS AND OTHER MEDICAL APPLICATIONS

The human body is a very hostile environment for an implant. Although the design of the implant can affect wear rates significantly, the choice of materials plays a key role in improving human implants. The problems related to the materials of the implants and the solutions for them developed in our laboratory are reviewed in Article II.

In an artificial hip implant, the sliding surfaces chafe against each other, and the whole implant and its adhesion interfaces are under heavy cyclic load. During the walking cycle the mass of the patient pivots and bounces on a surface of only a few square centimetres. Body fluids and the defence mechanisms of the body cause a sustainable corrosive load. For example, it has been shown that there are some 100000 particles emitted from the plastic cup part of a total hip replacement (THR) during each step [45] and that the surfaces of the cobalt-chromium-molybdenum (CoCrMo) parts dissolve tens of nanometers per year [46]. CoCrMo is the most common alloy used in articulating implants.

Mechanical and chemical stress can result in mechanical failure or detachment of the implant. The wear products provoke tissue reactions that may lead to aseptic loosening of the implant – the body begins to reject the implant. Almost all of the wear products of an implant have been shown to cause tissue reactions. Even those materials that are biocompatible in bulk, such as polyethylene, irritate the surrounding tissue when ground to small particles. The size of these insoluble particles triggers the defensive and protective mechanisms of the body [47,48]. However, this effect has not been found with diamond particles [49,50]. Entirely metallic implants wear less than hip joints with a plastic cup part, but the wear products are more aggressive. To put it very strongly, one could state that all of the wear products of an implant are noxious.

Our team has proven with numerous corrosion, pin-on-disk and hip simulator experiments that with ta-C coatings one can decrease the wear of implants significantly. These experiments not only imitate but also exceed the requirements of
Figure 11. Ta-C-coated hip joint: custom-made AISI316L acetabular cup-ball pair fitted on a commercial CoCrMo stem. Coating thickness on sliding surfaces is 10 µm. Thin ta-C coatings are bright and transparent, but when the coating thickness is increased, the appearance of the films becomes blackish mainly due to the graphite particles that pass the magnetic filter via multiple scattering. However, the quality of the film is not altered when coating thickness is increased.

the human body. The team has at its disposal the only internationally accredited hip simulator in Finland (Fig. 10). This simulator allows the systematic study of the combined effects of chafing, cyclic load and the surrounding fluid.

When the metallic ball and cup parts of an artificial hip joint are coated with a thick (>10 µm) ta-C film (Fig. 11), the wear resistance of the hip joint is improved by a factor of $10^6$ compared with uncoated conventional ones [51,52]. Figure 4 of Article II shows the profiles of a reference scratch before and after 2000000 walking cycles under a load of 500 kg. The difference in the profiles is barely measurable, although the scratch was made at the point of highest wear and the vertical resolution of the profilometer is 0.5 nm. The number of walking cycles roughly equals two years of walking of an average person. Similar results have been obtained in experiments of 15000000 walking cycles under a cyclic load with the maximum load reaching 300 kg. The tests were conducted according to ISO9225 standard procedure [52].

The coefficients of friction of ta-C-coated and natural hip joints are close to each other, and therefore, the overall stress on the implant is minimal [51,53]. This minimizes the risk of aseptic loosening related to the bending torque on fixation surfaces [53].

In addition to its hardness ta-C is chemically inert. This has been proven with enhanced hydrochloric and sulphuric acid corrosion tests conducted in our laboratory [53]. On a commonly used CoCrMo alloy, 1 µm of ta-C decreased the corrosion rate of the substrate by a factor of $10^5$ when exposed to a saline solution equivalent to the
Figure 12. Water jet cross cutter: (a) Schematic representation of a water jet cutter assembly, the gap piece is in sliding contact with the paper web (ER Scanner® [54]). (b) Ta-C-coated (10 µm) gap piece after 3000 km of testing in a light-weight coated (LWC) paper mill with a paper web speed of 100 km/h. The chafing of the paper has generated a groove diagonally across the contact ridge and the water hole. The shape of the groove is sharper after the hole because the water jet bends the edges of the paper. Because the coating got polished during the testing, the groove appears deeper in the photo than it actually is. For ta-C-coated gap pieces, the average groove-deepening rate at the point of the highest wear was less than 0.7 nm/km, whereas for WC-Co cemented carbide pieces it was 4000 times larger. The water jet was generated with 800 bar pressure through a 0.2 mm nozzle, yielding a water flow rate of 0.54 l/min [Article III].

Body fluid at 37°C for two years [51]. With thicker coatings, the corrosion can naturally be reduced more because the graphite particles and pinholes already in the film are covered with ta-C if the coating process is continued. Moreover, as an amorphous material, ta-C does not form long-range structures that could act as corrosion channels. It can also be argued that with thicker coatings the corrosion products can block long pores through the coating.

6. TA-C COATINGS IN INDUSTRY

According to our wear tests, ta-C is a superior protective coating material in both medical and industrial applications when it is used in an appropriate manner. Its only limitation is graphitisation and oxidation that begin at approximately 600°C in atmosphere. If chemically active substances are not present, the graphitisation temperature is higher. In a vacuum, diamond’s highest operating temperature is 1500°C [55]. Diamonds are not forever.

Although the emphasis of our research has been on medical applications, we have also worked in co-operation with the paper industry. The results of this effort are presented in Article III. The coated parts have been rather small key components of the system in question because the production capacity of our present experimental system is limited.

Applications in the paper industry have included support pieces of a water jet cutter and paper thickness, density and porosity probes (Figs 12 and 13). In all of these, the test pieces were in direct sliding contact with either the paper web or the
Figure 13. Porosity and basis weight probes: (a) Ta-C-coated ($\leq$5 µm) aluminium porosity measurement head slot plate (Microperm® [56]) after 6 months of testing at 100 km/h in a LWC paper mill. The slide slots are used to suck the plate towards the paper and to remove excess air, and the middle slot is used to draw air through the paper thus quantifying the porosity. (b) Porosity probe in action. (c) Basis weight probe (ER Scanner® [54]) during measurement (inside the circle). Because the measurement is done with X-rays, the probe has to be as close as possible to the target and the Ti or steel window has to be thin (50-100 µm). (d) Ta-C-coated ($\leq$10 µm) AISI316L basis weight probe protective window after 3 months of testing in sliding contact with the synthetic wire of a 100 km/h LWC paper mill. After long testing periods, both types of coated probes were in good shape, although the coatings were relatively thin due to the large size of the probes and the limited coating speed of our equipment. Some deep scratches were present on contact surfaces, but no delamination of the coating was observed, indicating that the adhesion of the coating was sufficient. It was also speculated that chafing against insulating ta-C generated static electricity and consequently micro discharges, causing part of the spot-like damages on the porosity probe (bright ring near the edge of the probe). Sap agglomeration on probe surfaces was diminished. It is noteworthy that uncoated probes wear out in periods as short as a few days [Article III].

wire in the paper machine. A rapidly moving paper web coated with oxides and carbides is like a giant grinding belt. In all the cases, the ta-C coating improved the wear resistance significantly, normally by a factor of several thousand. The anti-soiling properties of the sensors were also improved.

The results were as expected based on our earlier sand blasting experiments. When bombarded with aluminium oxide particles, our ta-C coatings outperformed commercial TiN coating (on stainless steel), synthetic ruby, WC-Co hard metal, sintered silicon carbide, sintered aluminium oxide and stainless steel (AISI316L and AISI440) [57]. Stuck on a 100 km/h travelling paper web, sand grains can destroy the coating and the sensor if the hardness, thickness and adhesion of the coating are insufficient.

Perhaps the clearest example of the superiority of ta-C has been the protection of paper paste viscometer nozzles (Fig. 14). With this kind of viscometer, one can simulate the conditions at the coating blade, which spreads the coating paste on the paper web. Measuring the shear rates ($10^7$ 1/s) required in future high-speed paper mills has been possible only with ta-C-coated viscometer slits. No other material has repeatedly withstood the stress generated during these measurements.
Figure 14. Coating paste viscometer slit: (a) Schematic representation of the coating paste spreading blade assembly. (b) Schematic representation of the cross-section of the viscometer slit (ACAV A2® [59]). (c) Ta-C-coated viscometer slit pieces. With ta-C-coated slit pieces, it has been possible to measure higher paste shear rates ($10^7$ 1/s) than with any other material combination [Article III].

Although hardness and strength are the qualities normally associated with ta-C, it also has other interesting properties. Because aluminium does not stick to a lathing tool coated with ta-C, normal deterioration of machining quality is avoided and lathing speed and accuracy can be multiplied [58]. Ta-C-coated lathing tools for aluminium are already in industrial production.

7. CONCLUSIONS AND DISCUSSION

Some 2000000 artificial joint operations world-wide are performed every year. Of these, more than 800000 are hip implant surgeries, 10000 of which are done in Finland [60]. It has been estimated that in the worst case up to one third of operations are revisions because the materials and consequently the implants are lacking [61].

If a total hip replacement operation with the implant costs approximately 8000 euros in Finland, one can estimate the cost of the failed implants. This sum does not include indirect costs such as sick leaves and surgical complications. Nor does this figure take into account human suffering.

Hip implant research at the University of Helsinki is gradually moving from in vitro wear testing towards biocompatibility research in vivo. The present generation of ta-C-coated hip implants undergoing tests in our laboratories has a modular structure, which means that the stem, ball and cup can be chosen individually for each patient. Unlike the earlier models that were custom-made for simulators and other wear testing, its design is suited for clinical use. Naturally, the number of cell culture tests is maximised to reduce the need for animal testing. Fortunately, hip implant testing is no more painful for animals than normal hip operations are for human beings. Moreover, the testing can be combined with, for example, routine hip operations in large dogs. However, organising post-operative follow-ups for pets can be problematic, and therefore, sheep are a more probable testing candidate.

Preliminary animal tests have shown that ta-C-coated implants have a positive biological response and their fixation is good [61,62]. Because ta-C does not wear, dissolve or react with bodily substances, we expect to see more results like this. If the research programme continues as planned and the funding is guaranteed, ta-C-coated implants could enter the mass markets in 5-10 years.

Our biomedical research combined with our experiences in industrial applications forms a solid base to expand the use of ta-C to other fields of mechanics.
The key to successful application of ta-C in extreme conditions is the method described in Article I, which shows that the adhesion problems of ta-C can be surmounted and that thick (>10 \(\mu\)m) high-quality ta-C coatings can be deposited provided that the substrate is chosen correctly and the plasma energy can be adjusted in an appropriate manner.

Our group was the first one capable to deposit thick high-quality ta-C films. When this was written our group was also the only one in the world capable of depositing these thick films.
NOMENCLATURE

Amorphous Diamond (AD or a-D) Popular name for high-quality ta-C coatings possessing properties similar to the natural diamond.

Aseptic loosening Detachment of an implant for a reason other than infection.

Acetabular Adjectival form of the word *acetabulum*, the upper part of the hip joint.

Basis weight Weight of a material covering a known area, grammage. Used instead of density for materials for which thickness is not well defined.

Chemical Vapour Deposition (CVD) Deposition method in which the gaseous deposit contains reactants that decompose and recombine to form the desired thin film. The reactants usually contain a chemically active precursor necessary for the film growth, e.g. hydrogen in the case of carbon. Decomposition and reaction are facilitated by having a heated substrate. Used for a variety of materials, e.g. polycrystalline diamond.

Diamond-Like Carbon (DLC) General name for films containing principally carbon and some diamond bondings.

Filtered Cathodic Vacuum Arc (FCVA) Physical vapour deposition method in which the deposit is ejected from the cathode by an arc discharge and the macroparticles are filtered from the deposit with a magnetic or electric field.

Filtered Pulsed Arc Discharge Deposition System (FPADDS) A variant of the FCVA method developed by the Helsinki University Diamond Group. In this end-window system, the operation is pulsed and the discharge current is led through a solenoid to generate the filtering magnetic field.

Physical Vapour Deposition (PVD) General name for deposition methods in which the atoms of the deposit are ejected in the vapour either by thermal evaporation or by atomic impact. Known methods are e.g. evaporation, sputtering and ion beam deposition.

Paper web Paper belt inside a paper machine, the paper product after the water extraction and before cutting. The full width of the paper sheet in the process of being formed, pressed, dried, finished and/or converted.

Tetrahedral Amorphous Carbon (ta-C) Amorphous pure carbon material that contains a large number (>70%) of sp³ hybridised diamond bondings.

Total Hip Replacement (THR) A prosthesis consisting of a stem, a ball and a cup that replaces the patient’s hip joint as a whole.

Tribology The science of friction, wear and lubrication.
**Whisker** A very thin, single crystal of high perfection, with an extremely large length-to-diameter ratio. Whiskers are used as the reinforcing phase in some composites [63].

**Wire (in a paper mill)** Woven belt made out of metal or synthetic wire on which the main part of the water is extracted from the paper slurry and the slurry is transformed into a paper web.
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