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Diamond-like carbon coating of alternative metal alloys for medical and surgical applications

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Abstract

The effectiveness of a plasma-deposited, diamond-like carbon (DLC) coating on aluminium alloy based surgical instruments is investigated. Surgical instruments must satisfy a number of important criteria including biocompatibility, functional performance, sterility and cleanability, structural integrity, and fatigue resistance. The integrity of the DLC layer and the diffusion barrier properties are of paramount importance due to biocompatibility considerations of the underlying aluminium metal. We investigate optimisation of the coating with incorporation of silicon and variation in negative self bias, and highlight the design and manufacture of a lightweight laparoscopic assist instrument from aluminium alloy coated with diamond-like carbon, which has been used successfully in the clinical environment to improve operations such as cholecystectomy (gall bladder removal) and exploratory techniques for the diagnosis of cancer.

1. Introduction

Multi-use surgical instruments are generally made from stainless steel or titanium alloys. These tough, stable materials bear a manufacturing cost burden and it would be advantageous if easier to manufacture materials were available. Aluminium alloys may have a significant role to play in this area, with the potential to reduce manufacturing costs and give ergonomic advantage to the surgeon due to a reduction in instrument mass. Weight and cost are important issues for retractors and device introduction instruments, for example. However, some parameters such as wear resistance, strength and biocompatibility have to be addressed to enable commonly used instruments to be manufactured from aluminium alloys.

There have been concerns about the biocompatibility of aluminium. Some studies suggest that aluminium leads to enhancement of neurodegeneration and is a potential risk factor in Alzheimer's Disease [1,2]. However, this remains controversial [3,4] and studies of metal workers demonstrate that short and long term exposure to high levels of aluminium increases concentrations of the metal in blood and urine, but this may not affect concentration of aluminium in the brain and does not necessarily show a detrimental effect on neurobehavioural performance [5]. The risk of any adverse effects related to aluminium biocompatibility could potentially be overcome by coating the instruments with a diffusion barrier. Diamond-like carbon (DLC) has demonstrated biocompatibility [6] and has been shown to be effective as a diffusion barrier, including for biomedical implants such as cardiovascular stents, heart valves and orthopaedic devices [7-10]. In addition to the barrier properties to prevent corrosion and leaching of aluminium to biological tissue, the damage resistance of the coating is also important in the clinical environment to counter wear and tear from normal operation and cleaning procedures. The relatively low surface friction can decrease biofilm adhesion and increase effectiveness of the post-operative cleaning regime [11].

Diamond-like carbon consists of sp^2 bonded (graphite-like) carbon within an sp^3 bonded (diamond-like) matrix, and can contain significant levels of hydrogen. Plasma enhanced chemical vapour deposition (PECVD) is a common laboratory technique to produce amorphous hydrogenated carbon thin films, including DLC. Control of PECVD deposition parameters affects the sp^2 / sp^3 ratio, hydrogen content and clustering of sp^2 sites, leading to film properties that can range from polymer-like to diamond-like [12]. Substrate treatment and interlayers have an effect on film adhesion, integrity, wear and corrosion properties [13,14]; incorporation of species such as N, O, F, Ar and Si within the film have been shown to affect the coating properties, including surface energy, topography, defect density, diffusion barrier efficacy and biomedical compatibility [10, 15-18].

In this work we demonstrate the use of a layered DLC based coating deposited on a prototype aluminium alloy surgical instrument, and examine the diffusion barrier and abrasion resistant properties of amorphous (silicated) carbons with various configurations.

2. Experimental

DLC films were deposited by RF PECVD process on a laparoscopic assist instrument manufactured from 6061-T651 (HE30) aluminium alloy. The final DLC layer was deposited with Ar:C_2H_2 ratio of 1:6 and bias voltage of 450V. Substrate cleaning, interlayers and transition layers were produced as described elsewhere [14], generating a film that has previously been shown to give good substrate adhesion, wear resistance and low friction coatings for machine tools [14].

Laboratory testing of different configurations of hydrogenated (silicated) amorphous carbon, a-C (:Si):H was conducted on aluminium substrates, cylindrical rods of 6mm diameter for diffusion barrier measurements and plates approximately 20x20mm for assessment of damage resistance. Trial experiments were conducted with a range of bias voltages and with the introduction of silicon to the final film as well as the interlayer. In this paper we show the variation of properties around a preliminary optimum. For all samples argon pretreatment with flow rate of 30 sccm, pressure of 8×10^{-2} torr and a bias voltage of 300 V was conducted for 20min. This was followed by an interlayer of a-C:H:Si deposited from tetramethylsilane (TMS) flow at 15sccm with bias voltage of 100V for 10 min. For the final film layer, deposited for 90min, the TMS: C_2H_2 ratio was varied from 0 to 42% with bias voltage at 200V, and the bias voltage varied from 100V to 300V with TMS: C_2H_2 ratio at 25%.

Diffusion barrier studies were conducted by immersing DLC coated aluminium rods in an aggressive sodium hydroxide solution, detecting mass loss from the sample and presence of aluminium in the solute. Samples were weighed and placed in individual containers with 80ml 10% solution NaOH in distilled water for 30min. Mass loss was calculated and the quantity of aluminium transferred to the solute measured utilising atomic absorption spectrometry. Each experiment was conducted in triplicate and mean values calculated.

Comparative measurements of random impact and abrasion resistance were conducted as a proxy for repeated instrument handling during and after surgical use. Test samples were mounted onto the walls of a neoprene rubber 0.85l chamber loaded with 365 g of triangular-form aluminium oxide particles, 5.25x5.25x6.25mm. The chamber was continuously rotated for one hour at approximately 50 rpm, causing impact and movement between test samples and abrasives. Samples were then ultrasonicated in acetone to remove loose particles before being placed in optical or scanning electron microscopy systems to analyze wear patterns, areas, and other features, compared to a control and other coated objects.

Water contact angles are calculated utilising an FTA1000B tensiometer from the mean values of at least twelve measurements of sessile drops; images were taken of multiple droplets, each of volume < 4 µl, at approximately 10 seconds from initial contact. Scanning electron microscopy images were collected in secondary electron and backscatter electron mode, without additional coating, utilising a Zeiss Supra 35VP field emission scanning electron microscope, operating with accelerating voltage from 5kV to 20kV.

3. Results and discussion

Figure 1 shows the DLC-coated aluminium assist instrument for use in laparoscopic (minimally invasive, or “keyhole”) surgery, and its use in a surgical procedure. The instrument was returned to the laboratory after three operations with autoclave sterilization processes (at approximately 137^{o}C) after each surgical procedure. Visual and light microscopy examination showed 16 visible small impact spot damage areas, typically a few hundred micrometres in size. These are heavily asymmetrically distributed over the instrument, and are predominantly located on one handle area. Scanning electron microscopy (SEM) examination, figure 2, confirmed these as impact damage, penetrating through the film and into the aluminium substrate (figure 2a). Away from these areas the coating integrity was not breached, either through fracture or delamination, and little debris adheres; figures 2b and 2c show representative areas, the features are primarily related to the finish of the aluminium. Figure 2d shows a higher magnification image of a linear feature related to the underlying substrate finish where some biological debris has been trapped; at the front left of this image is an area that has retained more debris which is related to partial removal of the film, likely an interlayer fracture. This is uncharacteristic of the film as a whole, two instances were found, both adjacent to a deep machining mark. This highlights that surface finish of the instrument prior to film deposition is an important factor, both in ensuring film integrity and in reducing any biological debris retention.

Trials of variation in coating processes were made in order to improve the efficacy of DLC coated Al alloys for biomedical tools. Of particular importance are adherence to the substrate and formation of an effective diffusion barrier to prevent metal ion release [8]. The use of an a-C:Si:H film/substrate interlayer has been used by a number of researchers to promote bonding and reduce adhesion failure

[7, 14-16]. Klages *et al.* [10] demonstrate efficacy of a-C:Si:H films as a diffusion barrier, and Maguire *et al.* [15], in their investigation of DLC coated stents and guidewires, show that doping the DLC with silicon further minimises film cracking and significantly improves corrosion resistance. Preliminary tests suggested a reduction of the bias voltage to 200V and incorporation of silicon into the film with a precursor ratio of TMS: C_2H_2 1:4 was most effective as a diffusion barrier. We show examination of variation of silicon content and substrate bias around this preliminary optimum. Figure 3 shows optical images of a-C(:Si):H coated aluminium after immersion in sodium hydroxide for 30 min, this is indicative of penetration of the NaOH through the barrier film and subsequent erosion of the aluminium alloy. Results of measurement of mass loss and aluminium transfer are shown in table 1. The incorporation of silicon into the film is of obvious importance, with the unsilicated a-C:H (figure 3 a) showing approximately ten times the degradation of the a-C:Si:H film deposited with a precursor ratio of TMS: C_2H_2 1:4. No further improvement was seen with increasing silicon content past this level. This improvement in barrier efficacy is also correlated with the hydrophobicity, the water contact angle increases from 72.1 ° to a maximum of 79.2° with the increase in the TMS: C_2H_2 ratio to 1:4. Reducing the bias voltage whilst maintaining the precursor ratio produces a film which shows further reduction in degradation by NaOH (figure 3 d), however, the aluminium transfer through the film appears to be increased, table 1. This may be related to a reduction in microscopic pinholes defects with reduced bias which will reduce corrosion [19,20], but the polymer-like nature of the film and reduction in density from around 1.9 gcm^{-3} to approximately 1.4 gcm^{-3} may reduce the barrier efficacy [10,12].

The variation of corrosion barrier effectiveness with silicon is consistent with work of Maguire *et al.* [15] who showed an increase in pore resistance of DLC-Si with increased Si content in electrochemical corrosion measurements. These researchers and Baia Neto *et al.* [21] investigated incorporation of silicon into PECVD-deposited amorphous hydrogenated carbon, and show a strong reduction in internal stress with increased silicon content. This was coupled with an almost constant film hardness and total hydrogen content [21], in contrast to Maguire *et al.* [15] who show increase in silicon content increases the hydrogen content and reduces film hardness. Both groups show increased sp^3 fraction resulting from silicon substitutionally incorporated into the amorphous network. Electron paramagnetic resonance and hydrogen effusion experiments [21] show microstructural changes in the films; an increase in silicon content results in a reduction in size and number of sp^2 clusters, coupled with an increase in voids. Maguire *et al.* [15] suggest the increasing impermeability is possibly due to reaction of oxygen at the pore origin forming SiO_x, but also show a significant decrease in DLC/substrate adhesion following prolonged immersion in biofluid, which they relate to fluid penetration through nanoscale voids or pores at a scale not detected by SEM measurements.

In addition to an effective diffusion barrier, damage resistance is also important, as confirmed by the examination of the prototype instrument. Figure 4 shows example SEM images of test pieces. Film damage was quantified by SEM examination in backscatter electron mode, which shows atomic number contrast. This enables consideration not only of film breach to the substrate, but also significant thinning, the damage from indent without fracture and interlayer fractures can be clearly seen figure 4d and figure 4b. Although predominant defect type changed from indent to partial fracture with increase in silicon precursor content, no significant change in surface damage defect concentration was seen. Changes in defect formation mechanism are visible in increasing bias voltage from 100 to 200 (figure 4) but no significant difference in concentration. Increasing bias voltage to 300V showed reduction of 65% in abrasion-induced defects consistent with increasing hardness of the film [12].

4. Conclusions

A layered thin-film structure of (silicated) diamond-like carbon (DLC) has been deposited on a surgical instrument manufactured from aluminium alloy. This has been successfully used in multiple operations with an autoclave sterilisation process between each use. Inspection and scanning electron microscopy examination of the instrument after use shows a general good response of the coating to operational processes. A small number of impact damage areas of order a few hundred micrometres in diameter were observed, except in these areas the coating integrity remains sound. There is some limited adherence of biological debris, which is associated with the machined finish on of aluminium.

Further development of the coating investigated the diffusion barrier properties and damage resistance as a function of deposition parameters. This showed the importance of a level of silication of the thin film in maintaining an adequate diffusion barrier. Reduction of the negative self bias to produce a more polymer-like film leads to reduction of the coating defects and increase in flexibility, but an apparent increase in permeability and a reduction in film hardness. This preliminary work suggests a coating deposited with bias voltage between 100V and 200V may be optimal for barrier properties, but sacrifices abrasion resistance.

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Figures and Table

Figure 1: DLC coated aluminium alloy laparoscopic assist instrument, adapted from [9]

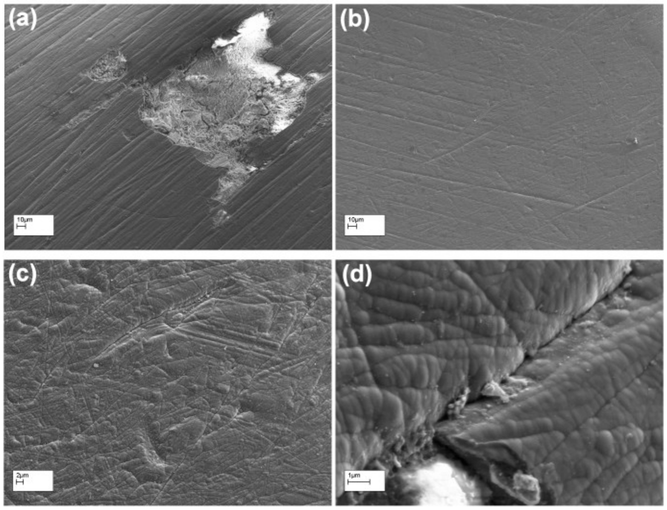

Figure 2: SEM images of salient features on DLC-coated aluminium instrument after multiple use. a) impact damage, b) and c) representative areas, d) trapped debris and partial fracture.

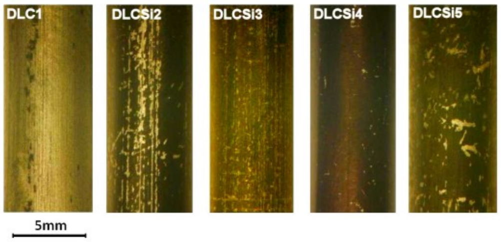

Figure 3: Optical images of DLC coated aluminium after NaOH testing; see table 1 for designation.

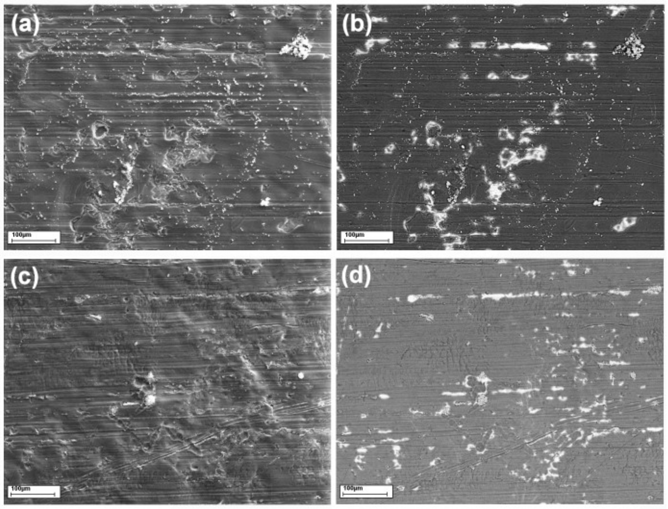

Figure 4: SEM secondary electron (a,c) and backscattered electron (b,d) images of coatings after damage resistance testing for sample DS2 (a,b) and DS4 (c,d).

label	**Deposition**		**mass loss** /mg	**solute** Al /ppm
	bias	**TMS/C_2H_2**		
DLC1	200	0	36±6	528±30
DLC-Si2	200	0.25	4±2	292±15
DLC-Si3	200	0.42	4±1	361±6
DLC-Si4	100	0.25	<3	386±42
DLC-Si5	300	0.25	7±3	442±25
No coating			56±3	615±31

Table 1: Sample designation, hydrophobicity and corrosion testing results