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Effects of pulse voltage and deposition time on the adhesion strength of graded metal/carbon films deposited on bendable stainless steel foils by hybrid cathodic arc – glow discharge plasma assisted chemical vapor deposition

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ABSTRACT

Graded Ti/C composite films with carbon topcoats are prepared on bendable stainless steel foils by hybrid cathodic arc / glow discharge plasma-assisted chemical vapor deposition to simulate cardiovascular stents. Strong adhesion between the stainless steel substrate and carbon topcoat is achieved due to the graded Ti/C interface and it is further improved by increasing the pulse voltage. Moreover, the graded coating is more hydrophilic than the stainless steel substrate.

1. Introduction

Stainless steels are used in cardiovascular devices such as stents [1,2]. A passive film with a thickness of a few nm's comprising oxides/hydroxides of Cr^{3+} and $Fe^{2+/3+}$ grows spontaneously on stainless steel in air and plays a vital role in the surface protection and corrosion resistance. However, interstitial fluids having 117 mM of Cl^-, blood plasma having 113 mM of Cl^-, and body fluids containing protein molecules and amino acids can attack stainless steels under in vivo conditions [3]. Consequently, metal ions can dissolve in body fluids [4,5] and after arterial injury, chemotactic and growth factors are released causing restenosis in stents leading to clinical consequences [6,7]. In this respect, surface modification is a viable approach to protect implant surfaces. For example, formation of TiO_2 layers by thermal oxidation [8], apatite layers by electrodeposition [9], ZrO_2 [10,11], ZrN [12], SiO_2 [13], and C [14] layers by plasma immersion ion implantation, as well as oxide layers by micro-arc oxidation [15] can effectively protect metal surfaces.

With regard to biocompatibility, it is desirable that the surface should immobilize protein molecules. Covalent immobilization of protein molecules on the surface while retaining their functions for a long period of time is important to biomedical implants and biosensors [16–19]. However, immobilizing protein molecules via weak interactions leads to detachment of protein molecules and unwanted conformational changes which affect the bioactivity of the implants. It can also produce deleterious effects such as inflammation, activation of cellular immune response, clotting, excessive fibrosis, and implant rejection. For instance, a strong inflammatory response has been detected from restenotic tissues after drug-eluting stent implantation and an inflammatory response has also been observed from bare metal stents [20]. To reduce the inflammatory response, efforts have been made to encapsulate implant surfaces exposed to blood with protein molecules but there are still failures [21], which may be ascribed to conformational changes (denaturation) in the protein molecules or insufficiently strong protein binding. All in all, an immobilized biomolecule with the native conformation preserved is essential to bio-recognition [22].

Carbon films are generally considered biocompatible [16,17]. In general, hydrophilic surfaces can preserve protein functions

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Table 1
Experimental parameters in plasma deposition of carbon films (C1 and C2) and Ti/C graded films with a top carbon layer (G1-G6).

S. No.	Sample ID	Substrate	Type of film	Bias Volt (kV)	C_2H_2 flow rate during Ti cathodic arc deposition (sccm /min)	CVD of C_2H_2		Total duration (min)
						Pressure (mTorr)	Duration (min)	
1.	C1	Stainless steel	Carbon film	−1.5		90	8	8
2.	C2			−3		90	8	8
3.	G1		Ti/C Graded film with a carbon topcoat	−1.5	0, 10, 20, 40, 60 & 80	90	8	14
4.	G2			−2	0, 10, 20, 40, 60 & 80	90	8	14
5.	G3			−2.5	0, 10, 20, 40, 60 & 80	90	8	14
6.	G4			−3	0, 10, 20, 40, 60 & 80	90	8	14
7.	G5			−3	0, 10, 20, 40, 60 & 80	90	3	9
8.	G6			−3	0, 10, 20, 40, 60 & 80	90	12	18

[23] but have low protein binding affinity [24]. Bilek et al. [16] demonstrated that carbon-based plasma-polymer-containing film covalently immobilized protein molecules while retaining their conformation on hydrophilic surfaces. The plasma-modified surface having mobile unpaired electrons are important to the formation of strong covalent binding with protein molecules [16]. Strong adhesion between carbon films and biomedical implants such as cardiovascular stents is imperative because the stents undergo deformation during implantation. Yin et al. [25] achieved strong adhesion of between 18 and 26 MPa by producing a graded interface between the carbon film and metal substrate and the plasma-modified carbon film exhibited good covalent immobilization of protein molecules. Jamesh et al. [18] accomplished strong adhesion by fabricating a graded interface between the carbon film and metal substrate using hybrid cathodic arc / glow discharge plasma-assisted chemical vapor deposition (PACVD). Cathodic arc deposition is suitable for the deposition of metal films [26,27] because the cathodic arc produces an abundant amount of ions and the electron density in the cathodic plasma can be as large as 10^{20} cm^{-3} [28]. Cathodic arc deposition utilizing beam energies between 20 eV and ~500 eV is suitable for the fabrication of amorphous carbon films with 80% tetrahedral bonding [29] and with tetrahedral coordination with a nearest neighbor distance of 1.53 Å, coordination number of 4, and bond angle of 110° [30]. Furthermore, the graded film prepared by cathodic arc deposition exhibits good covalent binding of protein molecules in addition to strong adhesion [18], and good cytocompatibility and improved corrosion resistance have been observed from graded films prepared by hybrid cathodic arc – glow discharge PACVD [31]. However, the dependence of the adhesion strength on the plasma processing parameters has not been previously determined. The objective of the present work is to determine the effects of the plasma conditions in hybrid cathodic arc – glow discharge PACVD such as the pulse voltage and deposition time on the adhesion strength of Ti/C graded films deposited on flexible stainless steel substrates.

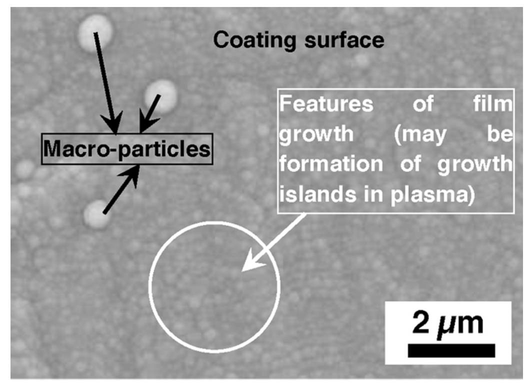

Fig. 1. Surface morphology of the G4 Ti/C graded films with a carbon topcoat on stainless steel.

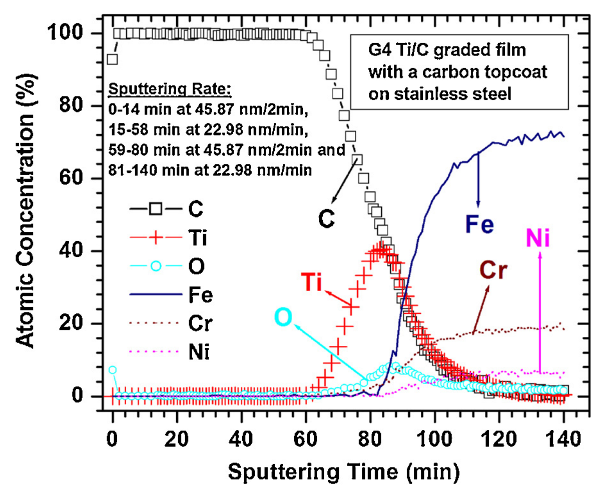

Fig. 2. XPS depth profile of G4.

2. Methods and materials

2.1. Plasma deposition processes

The films were prepared by a hybrid process involving deposition of Ti by filtered cathodic arc deposition and C by PACVD. Two types of films were investigated: monolayer C films, and composite films with a graded Ti/C first layer and C topcoat. The monolayer C films were deposited by only PACVD whereas the composite films were produced by a combination of cathodic arc deposition and PACVD.

In the cathodic arc deposition part of the process, the Ti plasma was generated by a 99.998% pure Ti cathode at a high current (60 A). The cathodic spots produced a highly ionized Ti plasma contaminated by Ti macro-particles. The macro-particles and the few neutral atoms were removed from the plasma stream by a curved magnetic solenoid filter [32]. The Ti film properties were improved by negatively pulse-biasing the substrate between −1.5 and −3 kV (2.5 kHz pulse repetition rate and 30 μs pulse width) via a 2.5 m coaxial cable. Further details about the cathodic arc chamber were reported previously [30,33,34]. The PACVD part of the process used a glow discharge sustained in C_2H_2 between the 300 mm diameter grounded chamber which served as the anode and an 80 mm diameter steel disk substrate holder serving as the cathode. The same pulsed high voltage power supply described above was used to power the glow discharge. A mass flow controller regulated the C_2H_2 gas flow rate and before deposition, the base pressure of the vacuum system was about 10^{-6} Torr. The films were deposited on 25 μm thick 316L stainless steel foils (Fe, <0.03% C, 16–18.5% Cr,