ADHESION CHARACTERISTICS OF THIN VACUUM DEPOSITED CARBON FILMS

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I. INTRODUCTION

In recent years, highly favorable results have been obtained using low temperature isotropic (LTI) pyrolytic carbons in prosthetic devices requiring a high degree of thromboresistance.[1] The development of vacuum-deposited carbon films was undertaken to extend the application of carbon to geometries and configurations that can not reasonably be fabricated from LTI carbon. The structural, physical and compositional characteristics of vacuum deposited carbon films have been found to be similar to LTI carbon.[2,3]

Thin carbon films have been produced on complex shaped metallic and polymeric bio-implant devices. To be truly useful, however, these films must bond well to the substrate and show good adhesion in service. The bond strength, interfacial characteristics and fracture mechanisms are, therefore, important considerations for successful applications of these films.

Thin film adhesion can be divided into several types: (a) interfacial or monolayer adhesion in which the film and the substrate meet at a well defined boundary is characterized by an abrupt change from the film material to the substrate material in distance on the order of a monolayer thickness; (b) interdiffusion adhesion in which there is a gradual change in composition across the interfacial region which may be several hundred angstroms thick provided there is some solubility of the film and substrate and there is sufficient driving energy to promote diffusion; (c) intermediate layer adhesion due to compound formation at the interface and (d) mechanical adhesion due to interlocking of the film and substrate due to surface roughness. In most cases, the actual adhesion is a result of several of the above types. The most desirable type of interface, from the standpoint of adhesion, is one in which stresses in the interfacial region are distributed over an appreciable volume. This can best be done by grading the composition of the interface from that of the substrate material to that of the coating material. The purpose of this study was to examine the interfacial characteristics of as-deposited carbon films on two different metallic substrates and to determine the obtainable bond strength of carbon films on metallic and polymeric materials.

II. EXPERIMENTAL

Vacuum deposition was used to deposit thin carbon films (~ 4000Å) on metallic and polymeric substrates. The coating apparatus and deposition technique have been described previously.[2] The substrates were sputter-cleaned by inert gas ion bombardment before film deposition and ion bombardment was continued during deposition. The substrate voltage was varied from 1.8 to 4.0 KV, while the argon pressure and deposition rate were kept constant 5 x 10^{-3} torr and 10A/sec, respectively. The metallic substrates (stainless steel and titanium) consisted of highly polished discs 0.25 inch in diameter and 0.005 inch thick. The polymeric substrate (Vespel-a polyimide) consisted of small cylinders 0.25 inch in a diameter and 0.5 inch long.

Epoxy resin was used to cement the metallic test specimen carefully between identical stainless rods and cured for 48 hrs. The rods were grooved near the ends to promote film debonding somewhere inside the film and not at the edge, so that a true bond strength and not a tearing or peeling strength could be measured. A precision fixture and ball joints used to assure a tensile force normal to the film and along the axes of the rods. Tests were conducted on a standard Instron with a crosshead speed of 0.02 in/min. In the case of polymer test specimens, one end was threaded to provide a good grip while other end was polished before film deposition.

An Auger electron spectroscopy system[4] that employs an in-site ion beam sputtering gun was used for composition depth profiling through the film and for probing the interface. Peak-to-peak heights for carbon and substrate elements were multiplexed and recorded as a function of sputtering time. A complete spectrum was periodically obtained through the film and interfacial region.

III RESULTS AND DISCUSSION

Table I lists the experimental conditions and average bond strengths measured from at least six identical specimens of different substrate materials. Considerable effort was spend in maximizing the adhesive strength of different cements available but nevertheless, in several cases, debonding occured not at the film-substrate interface but at the cement/substrate interface.

Bond strength greater than 5100 psi were achieved for both carbon/stainless steel and carbon/titanium systems. All substrates were sputter cleaned under identical plasma conditions and substrate bias voltage was adjusted to different values during film formation. Excellent adhesion obtained on stainless steel substrate under all conditions indicates ease of thin carbide layer formation at the interface at temperatures as low as 100°C. At higher bias conditions and therefore higher substrates temperatures (>400°C), larger thermal stresses may have contributed to somewhat reduced bond strength. The formation of carbide layer was confirmed by Auger spectroscopy (Fig. 2) and is probably due to effective ion-bombardment cleaning of the substrate which is exposed to highly reactive (partially ionized) carbon vapor during film deposition.

In case of titanium substrates, bond strength increased with higher bias voltage and substrate temperature. These substrates showed higher oxygen concentration at the interface and therefore required somewhat larger activation (higher substrate temperature) for the formation of a carbide layer at the interface. Auger Spectra confirmed the formation of titanium carbide layer at the interface.[5] The thickness of interfacial region in both stainless steel and titanium substrates was estimated to be of the order of a few hundred Angstroms (~ 200-300°A).

TABLE I
BOND STRENGTH OF THIN CARBON FILMS OF STAINLESS STEEL, TITANIUM AND VESPEL SUBSTRATES

Substrate Type	Bias Voltage (KV)	Bond Strength (psi)[a]	Debonded Interface
Vespel	1.6	=2860 ± 383	Film/Substrate
Stainless	1.8	>4957 ± 550	Cement/Substrate
Titanium	1.8	=1569 ± 203	Film/Substrate
Vespel	1.8	=3399 ± 587	Film/Substrate
Vespel	2.0	=3718 ± 1069	Film/Substrate
Vespel	2.2	(b)	(b)
Vespel	2.4	(b)	(b)
Stainless	2.5	>4237 ± 390	Cement/Substrate
Titanium	2.5	=3952 ± 383	Film/Substrate
Stainless	3.0	>4563 ± 305	Cement/Substrate
Titanium	3.0	>5174 ± 331	Cement/Substrate
Stainless	3.5	=5113 ± 462	Film/Substrate
Titanium	3.5	>4258 ± 253	Cement/Substrate
Stainless	4.0	=5297 ± 469	Film/Substrate
Titanium	4.0	=4157 ± 420	Film/Substrate

(a) Average of six tests or more (± standard deviation)
(b) Failure occured in the bulk polymer.

The polymer substrate were treated in a weak plasma before film deposition at several substrate bias voltages. Averages bond strengths of more than 3000 psi were measured on most specimens except where the failure occured in the bulk polymer itself. The nature of interfacial region in polymer-carbon system was not examined but is speculated that C - C type bonding may have been established between carbon film and substrate.

CONCLUSIONS

(a) Vacuum deposited thin carbon films adhere strongly to metallic (stainless and titanium) and polymer (Vespel) substrates. The bond strengths are comparable to those achievable with the best available structural adhesives.[6]

(b) Interfacial examination reveals a thin compound layer formation which should ensure good adhesion of carbon films on metallic implant devices.

Supported in part by NIH contract NO1-HV-4-2928.

References

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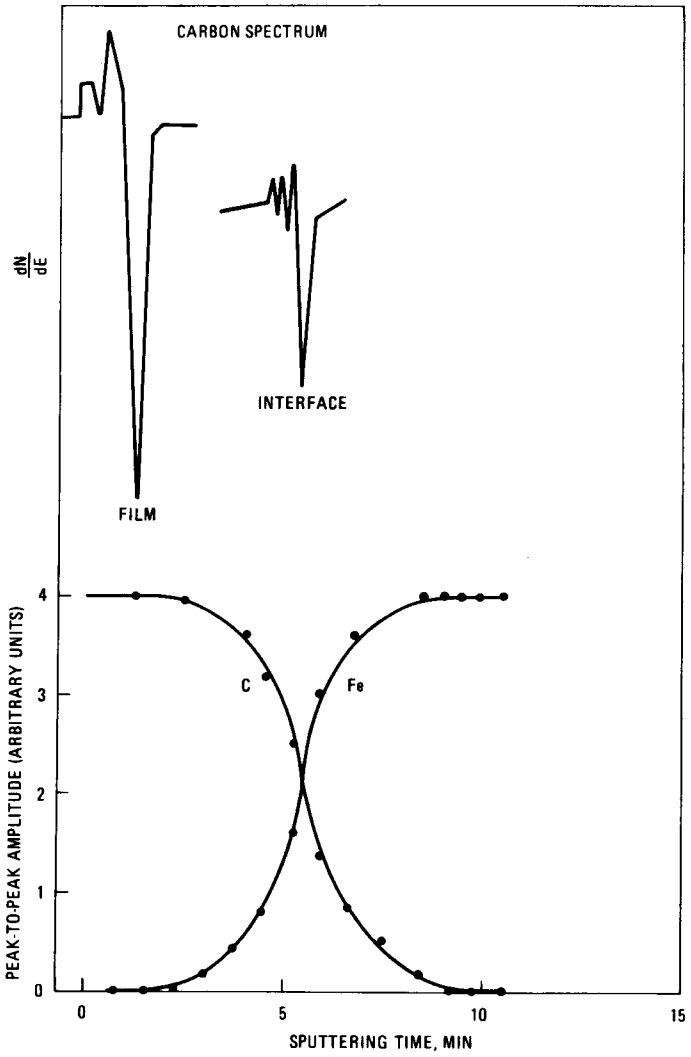

Fig. 1 - Auger depth profile of carbon/stainless steel interface. The change in the shape of carbon spectrum shown at the top is indicative of carbide formation at the interface.

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