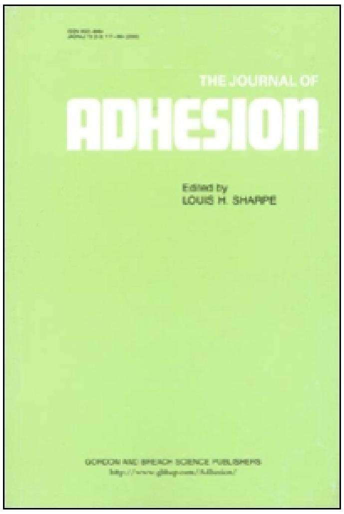

**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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**To cite this Article** Deshayes, L. , Charbonnier, M. , Prakash, N. S. and Romand, M.(1993) 'Adhesion Measurement of Amorphous C : H Films Deposited onto Stainless Steel. Spectroscopic Investigation of Interfaces', The Journal of Adhesion, 43: 3, 209 — 221
**To link to this Article: DOI:** 10.1080/00218469308026600
**URL:** http://dx.doi.org/10.1080/00218469308026600

*J. Adhesion*, 1993, Vol. 43, pp. 209–221
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Printed in the United States of America

# Adhesion Measurement of Amorphous C : H Films Deposited onto Stainless Steel. Spectroscopic Investigation of Interfaces

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*(Received April 8, 1993; in final form August 2, 1993)*

Amorphous hydrogenated carbon films obtained by the Plasma Assisted Chemical Vapor Deposition (PACVD) process, have been extensively studied by many authors[1,2,3] because of their interesting properties (hardness, optical transparency, chemical inertness, high electrical resistivity). In the present work, carbon films were deposited on stainless steel from glow-discharge polymerization of methane at reduced pressure, using an RF generator operating at 13.56 MHz.

These thin protective films are able to play the role of a primer to which another polymer (adhesive, paint, lacquer . . .) can subsequently be adhered. Surface treatments of the substrate and of the polymeric film were developed in order to obtain suitable adhesion properties, firstly of the film on the metal substrate, secondly of an adhesive on the hydrogenated carbon film. These treatments were monitored by two spectroscopic methods, *viz.* X-ray photoelectron spectroscopy (XPS) and (Low Energy Electron Induced X-ray Spectrometry) (LEEIXS). Mechanical measurements were made using a three-point flexure test[4] (Norm AFNOR T 30 010).

KEY WORDS hydrogenated carbon films; plasma assisted chemical vapor deposition (PACVD); XPS; LEEIXS; mechanical measurement; three-point bend test; primer; plasma polymerization; functionalization of surfaces.

## INTRODUCTION

The ability to deposit amorphous hydrogenated carbon (a-C : H) films on metallic substrates presents a high degree of technological interest as such chemically inert films could play the dual roles of adhesion primer and anti-corrosion barrier. In this work, such films were deposited onto stainless steel substrates by a "plasma polymerization" process. It should be noted that during such a process an electrical discharge takes place in a polymerizable gas (or mixture of gases) which leads to the formation of a thin film on the substrate surfaces exposed to the discharge. Adhesion of such films to the substrate was studied as a function of different deposi-

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tion parameters. In order to gain a proper understanding of interface phenomena, different surface analyses were carried out.

## EXPERIMENTAL

### Materials

The stainless steel substrates used were industrial quality F 17 sheets of 0.5 mm thickness. Plates measuring 50 × 10 mm were stamped out and used after surface treatment and film deposition to prepare specimens for adhesion testing. The adhesive used for setting up such testing was a two-part epoxy resin (3525-B/A from 3M).

### Plasma Treatments

These were performed in a cylindrical reactor from Plasma Technology (model RI E 80). This system consists of two parallel electrodes (4 cm apart, 17 cm in diameter). It is fed by an inductively-coupled power source operating in the 0–300 W range at a radio frequency of 13.56 MHz. Gas flow can vary from 0 to 50 scc/m and the pressure inside the reactor from 0.1 to 200 mTorr.

An appropriate treatment of the film surface for developing strong adhesion between film and adhesive is necessary for measuring film/substrate adhesion with the three-point flexure test. Therefore, a part of this work was devoted to the surface treatments of both substrate and film. All of them were carried out by a plasma process. Typically, the different steps of a sample deposition were the following:

—the substrate, previously degreased with acetone in an ultrasonic bath, was etched and functionalized by a plasma treatment in $O_2$, $NH_3$ or Ar at reduced pressure (gas flow: 30 scc/m, gas pressure: 50 mTorr, generator power: 120 W, treatment duration: 5 min).

—after pumping down to 0.1 mTorr, the reactor was filled with $CH_4$ for the film deposition step. The deposition parameters we have chosen for obtaining coatings variable in thickness, composition, structure and cohesion are gas pressure (10 to 150 mTorr), generator power (10 to 250 W) and deposit duration (10 to 60 min).

—after film deposition the reactor was pumped down again to 0.1 mTorr, then filled with $O_2$ or $NH_3$ for the film functionalization step which is of prime importance because hydrogenated carbon films have no natural tendency for chemical bonding. This operation was carried out by a mild plasma treatment under the following conditions: (gas flow: 30 scc/m, gas pressure: 50 mTorr, generator power: 120 W, treatment duration: 12s). Then, the epoxy adhesive was deposited on the samples within four hours of plasma treatment.

### Analysis Methods

X-ray Photoelectron Spectrometry measurements were carried out on a RIBER SIA 200 instrument using a MAC 2 analyser. Samples to be analysed were always introduced in the analysis chamber within a few minutes of plasma treatment in order to limit contamination. Sprectra were obtained using non-monochromatic X-ray sources (MgKα at 1253.6 eV or AlKα at 1486.6 eV) and resolution of 2.3 eV for survey spectra and 0.9 eV for high-resolution spectra. During analysis, the chamber pressure was maintained below $1 \times 10^{-9}$ Torr. The analyses were carried out at a take-off angle of either 70 or 25° with respect to the surface, on $1 \times 1.2$ cm rectangular samples. All the observed photopeaks were corrected for charging effects to the hydrocarbon species value at 284.6 eV.

Low Energy Electron Induced X-Ray Spectrometry measurements were carried out on a wavelength-dispersive X-ray spectrometer using an electronically-stabilized gas discharge tube which operates as an electron source under the primary vacuum of the spectrometer. Typical operating conditions are in the 1–5 kV range with a current between 0.1 and 0.2 mA, the diameter of the electron beam at the sample surface being less than 1 $cm^2$. Soft and ultra-soft X-rays emitted in such conditions, and particularly K radiations from light elements, are dispersed by flat analyzing devices and detected by a flow proportional counter. Details about this technique are given in the literature.[5–7] It need only be recalled that this tool is capable of probing the surface and near surface of materials typically in the 5 to 200 nm range, the corresponding depth depending, among other parameters, on the incident electron beam energy and the nature of the sample. In the following, the method is used for measuring the carbon film thicknesses. For that, it is calibrated in comparison with a gravimetric method using a balance sensitive to a microgram.

## Adhesion Testing

Adhesion testing was carried out using a three-point flexure method according to the AFNOR T 30 010. It should be mentioned here that this test has already shown its potential, not only in evaluating the effects of various adherend treatments, but also in optimizing, for a given treatment, the experimental conditions to be chosen in order to produce better adhesion. The adherend/adhesive specimen geometry used has previously been described.[4] The bonded specimens were submitted to curing for 2 hours, at 80°C, stored for 24 hours in a controlled atmosphere (20°C at 50% RH) then tested. The testing machine (Flex 3 from Techmetal, France) maintained the cross-head displacement at a rate of 0.5 mm $min^{-1}$, recorded the conventional load/displacement curve and determined the parameters of interest. In this work, the adhesion properties of the systems investigated were determined by numerical integration, up to the ultimate displacement value, of the area comprised between the load/displacement curves of the coated substrate/adhesive system and the coated substrate alone, respectively.[8] This area gives the failure initiation energy (in mJ) of the bonded joints and provides a relative indication of the bond strength at (and near) the substrate/film interface. It, therefore, allows one to compare the effects of various adherend treatments and of the characteristics of the film itself. In each case, a series of six specimens were studied in order to obtain statistical reproducibility. In each figure providing adhesion data, results for each series are represented by a rectangle whose height indicates the statistical error and whose central point indicates the average value.

## RESULTS AND DISCUSSION

### XPS and LEEIXS Analyses of Plasma-treated Surfaces

Surface treatment of the substrate before coating is necessary to allow good adhesion of the film. The results of plasma substrate cleaning and activation are shown in Figure 1 which represents XPS survey spectra of the following samples: (a) degreased, (b) degreased then $O_2$ plasma treated, (c) degreased then $NH_3$ plasma treated, (d) degreased then Ar plasma treated. As indicated in the literature,[9,10] all the plasma treatments lower surface carbon contamination. Oxygen plasma decreases Cr content at the surface, argon plasma increases that of Cr, Fe and O, while ammonia plasma, which does not modify the relative proportions of these elements, brings nitrogen atoms to the surface probably in the form of NH or $NH_2$ groups as shown by FTIR.[11] The increased oxygen signal in the case of argon plasma is the result of the very reactive surface of the sample being oxidised after exposure to ambient atmosphere before XPS analysis. Therefore, as the substrate is maintained in the plasma chamber under inert atmosphere before coating, its surface is not very likely to contain reactive oxygen. The activation of the stainless steel surface either by $O_2$ plasma (fixation of reactive oxygen atoms) or by $NH_3$ plasma (fixation of nitrogenated groups) allows a good adhesion of the carbon film compared with the results obtained with more traditional surface treatments (chemical etching). Figure 2 shows, for different surface treatments, the energy required to

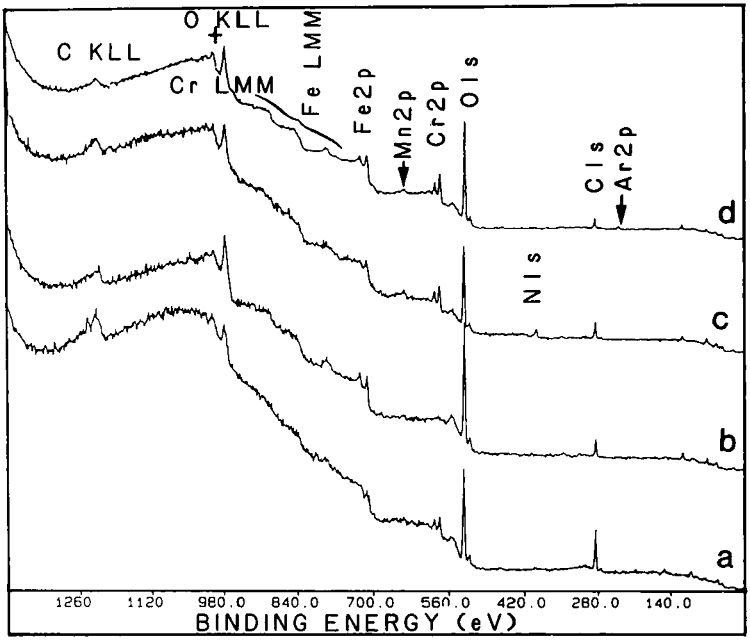


FIGURE 1 XPS survey scans (X-ray source: AlK$\alpha$) of a stainless steel substrate: (a) degreased, degreased then (b) $O_2$, (c) $NH_3$, and (d) Ar plasma treated.

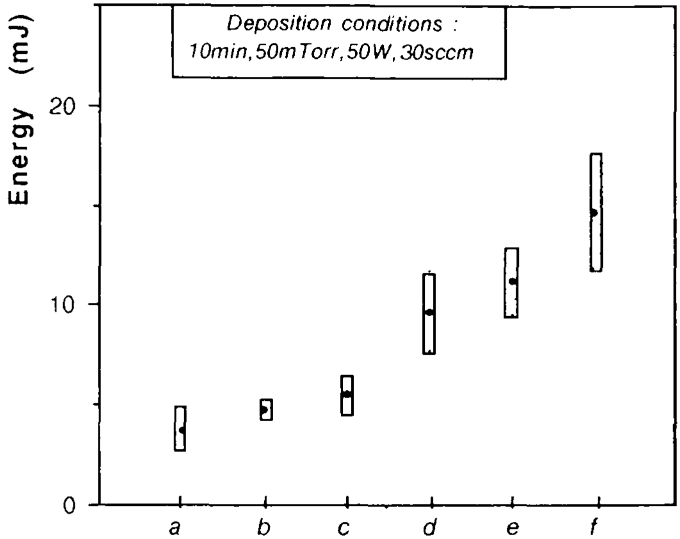
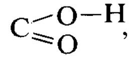


FIGURE 2 Adhesion properties of carbon films *versus* different surface treatments of the substrate: (a) degreased then sand-blasted, degreased then (b) Ar plasma treated, (c) chemically treated in a HF/HNO$_3$ bath, (d) ultrasonically degreased, (e) O$_2$ plasma treated, (f) NH$_3$ plasma treated.

delaminate the samples at the film/metal interface. The NH$_3$ plasma treatment of the substrate surface provides the best performance. Improvement of the film/metal interface quality could be explained by the fact that nitrogen at the metal surface and carbon from the a-C : H film both have a natural trend towards tetrahedral coordination which would avoid a sharp transition between two very different chemical phases.

Secondly, surface treatment of the polymer is necessary to ensure chemical bonding between a-C : H film and adhesive for setting up the mechanical test. Indeed, because of its chemical inertness, the hydrogenated carbon film has no natural tendency to establish chemical bonds with another material and, therefore, must be functionalized.[12,13] The results of amorphous carbon film functionalization by O$_2$ and NH$_3$ plasma are represented in Figure 3 which shows XPS survey spectra of samples without treatment (a), with NH$_3$ (b), and O$_2$ (c) plasma treatments. Spectrum (a) shows that there is some oxygen on the carbon film surface. This oxygen is only fixed on the surface after exposure to air. Oxygen plasma introduces a large content of oxygen to the surface while ammonia plasma favours nitrogen fixation, the presence of oxygen being also due to atmospheric exposure. In order to determine specifically the nature of the functional groups created by the treatments, C 1s spectra were recorded with a grazing take-off angle (Figure 4). Oxygen plasma treatment (Figure 4b) creates essentially  $C\begin{smallmatrix}\nearrow O-H\\ \searrow\!\!= O\end{smallmatrix}$, C=O and C—OH groups. Ammonia plasma forms mainly C—N bonds (Figure 4a), the corresponding photopeak being shifted of 1 eV in comparison with the main C 1s photopeak.[14] The presence of these C—N bonds is suggested in the spectrum by the broadening

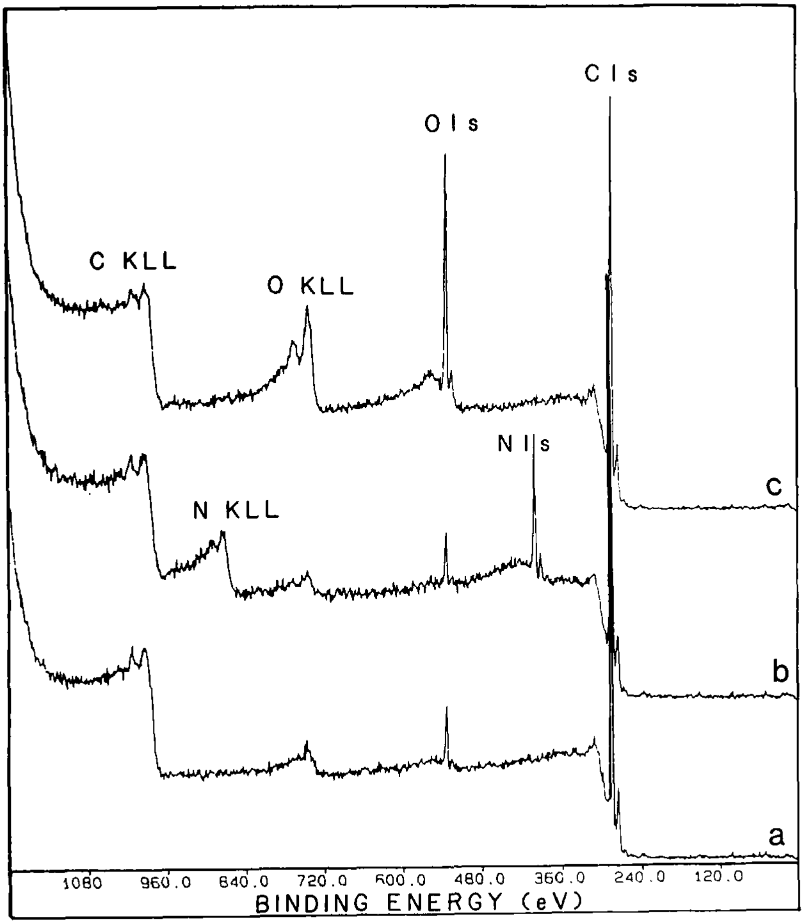


FIGURE 3 XPS survey scans (X-ray source: MgK$\alpha$) of carbon films (a) without treatment, functionalized by (b) $NH_3$, and (c) $O_2$ plasma treatment.

of the C 1s peak towards higher binding energy, hence increasing the full width-at-half-maximum (FWHM). This increase is also partly due to C—OH and C=O groups which appear after air exposure. It is very likely that $NH_x$ groups fixed on the film surface play an important role in adhesion of the epoxy resin. As a comparison, the C 1s photopeak obtained after argon plasma treatment (Figure 4c) presents the lower FWHM. However, a slight broadening towards higher binding energy is observed. It is mainly due to C—OH and C=O groups resulting from air exposure before XPS anlaysis. In addition, it should be noted that during the plasma treatment of the amorphous carbon films there is competition between functionalization and etching.[12,13,15] The former has just been shown by XPS analyses, the latter which varies film thickness can be controlled by LEEIXS mesurements,[5-7] by following the intensity variation of the CK$\alpha$ radiation emitted by the film and the FeL$\alpha$ radiation emitted by the substrate, as a function of $O_2$ and $NH_3$ plasma duration. In these experiments incident electron beam energy was 4 keV. CK$\alpha$ radiations were

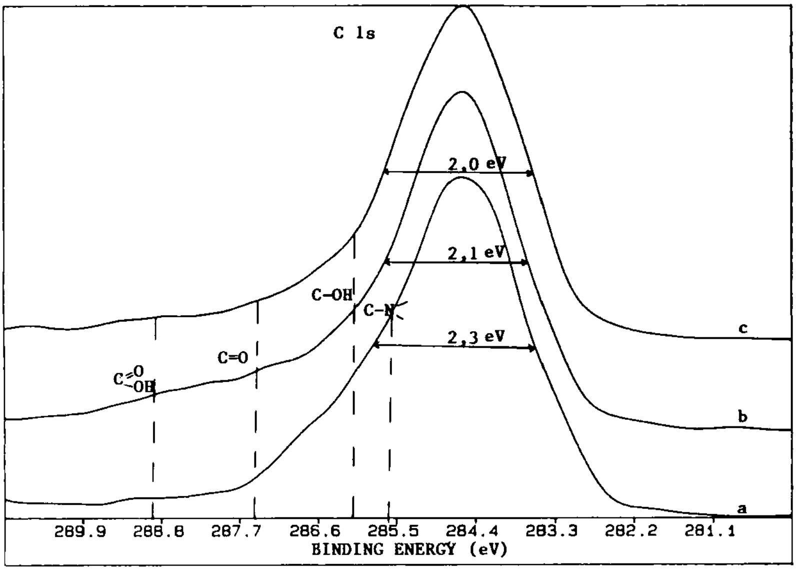


FIGURE 4 C 1s spectra (X-ray source: MgK$\alpha$) of (a) an $NH_3$, (b) an $O_2$, (c) an Ar plasma treated carbon film.

dispersed with an OHM crystal (2d = 6.3 nm) and FeL$\alpha$,$\beta$ with a TlAP crystal (2d = 2.574 nm). As etching increases, the CK$\alpha$ intensity decreases, whereas the FeL$\alpha$ intensity increases. All these experiments were performed on films of identical thickness (about 80 nm). Figure 5 shows that $O_2$ plasma produces a much stronger etching than $NH_3$ plasma. Therefore, the latter was further used to functionalize

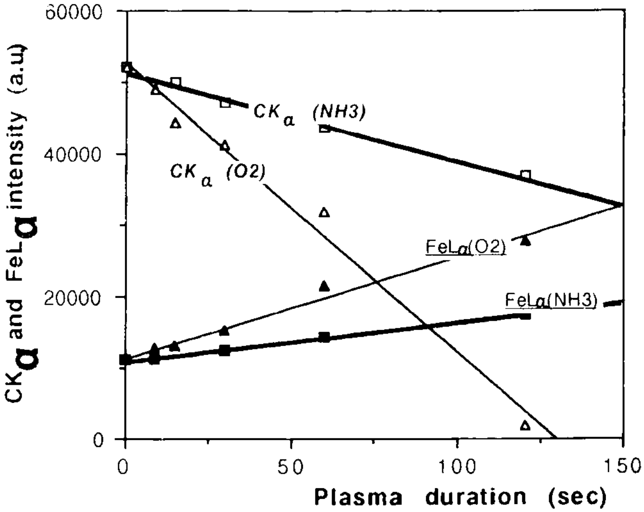


FIGURE 5 Intensity variation of CK$\alpha$ and FeL$\alpha$ measured by LEEIXS *versus* $O_2$ and $NH_3$ plasma duration.

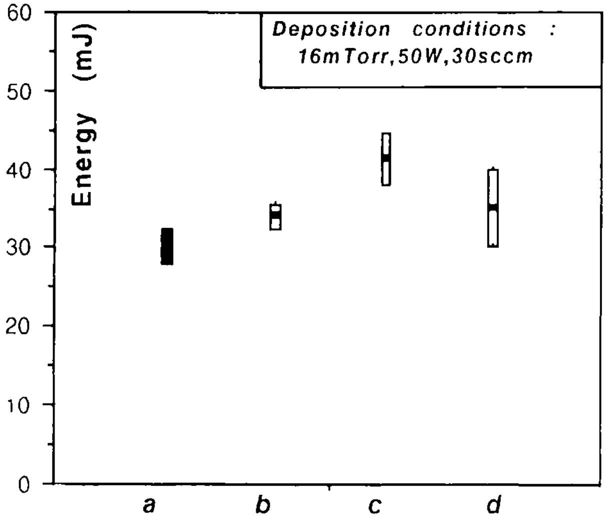


FIGURE 6 Failure initiation energy of the system as a function of the film surface treatment: (a) without treatment, (b) $O_2$, (c) $NH_3$, (d) $N_2$ plasma treated (an adhesive failure at the film/substrate interface is represented by an empty rectangle and at the adhesive/carbon film interface by a solid rectangle. The same symbolism is used for all the following figures).

the film. Figure 6 gives the comparative results of the adhesion measurements for plasma-treated and untreated samples. Without treatment, failure takes place at the adhesive/film interface which does not allow the measurement of the film/substrate adhesion. However, with a plasma treatment of the film, failure always takes place at the film/substrate interface and for somewhat different failure initiation energy levels, whereas they should, theoretically, be identical. Indeed, the tested systems differ only by the film surface treatment.

## Adhesion Measurements

Many authors have studied amorphous carbon films, but few have concentrated on their adhesion properties. Mechanical tests used, particularly the scratch test,[16,17] are not well-suited to quantify the adhesion of a film to its substrate. Indeed, the critical load for which a clear track is formed depends, among other factors, on whether the film is ductile or brittle.[18] In other words, it depends on the intrinsic properties of the film and not specifically on the quality of the film/substrate interface. In addition, many workers have carried out wettability measurements on this kind of film[10,19] with the aim of improving surface energy.

Different series of films were prepared according to various experimental conditions to ensure the production of films of uniform and stated thickness. The different plasma variables (pressure, gas flow rate, generator power and treatment time) were rigorously controlled. The thickness calibration, particularly *versus* treatment time, was performed in a gravimetric way. Film adhesion measurements were carried out by the three-point flexure test. In the following figures, blackened rectangles indicate that delamination occurs at the carbon/film adhesive interface. In this case, film/adhesive adhesion is lower than film/substrate adhesion and the latter cannot, therefore, be measured. It is to be noted that failure location was identified by Electron Microprobe Analysis or by Infra-Red Reflection Absorption Microscopy.

Figures 7 a and b concern samples deposited at variable power but, respectively, under a pressure of 20 and 50 mTorr. The lower the power used to prepare the film and, therefore, the lower its thickness, the better the film substrate adhesion. In both cases, for a power of 20 W, carbon film is not stripped off, delamination taking

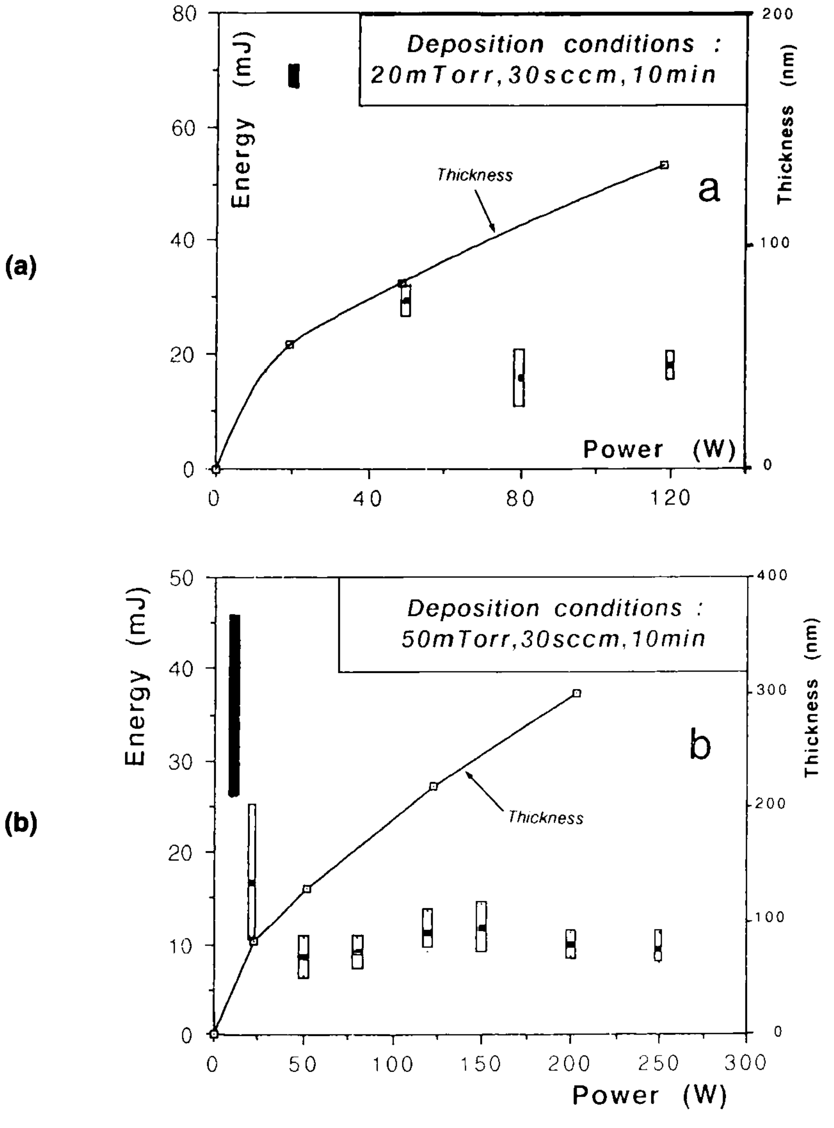


FIGURE 7 Adhesion properties for carbon films elaborated at variable power under (a) 20 mTorr, (b) 50 mTorr.

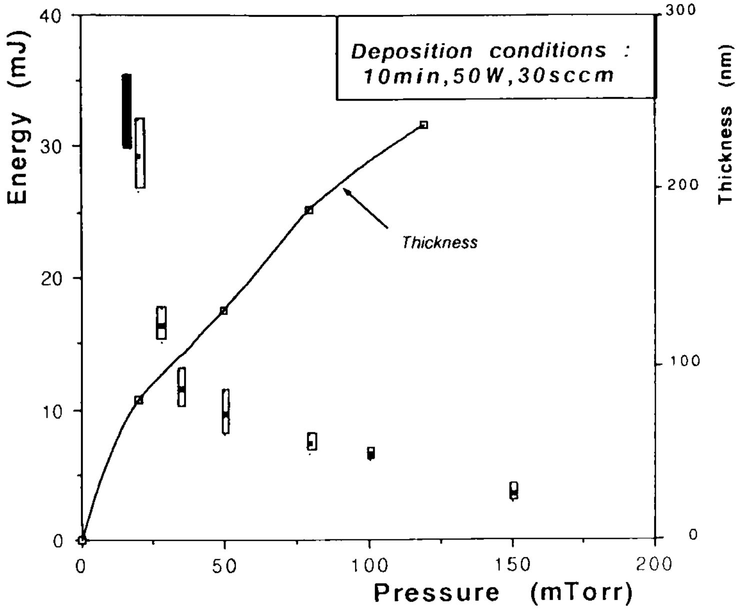


FIGURE 8 Adhesion properties of carbon films elaborated at variable pressure.

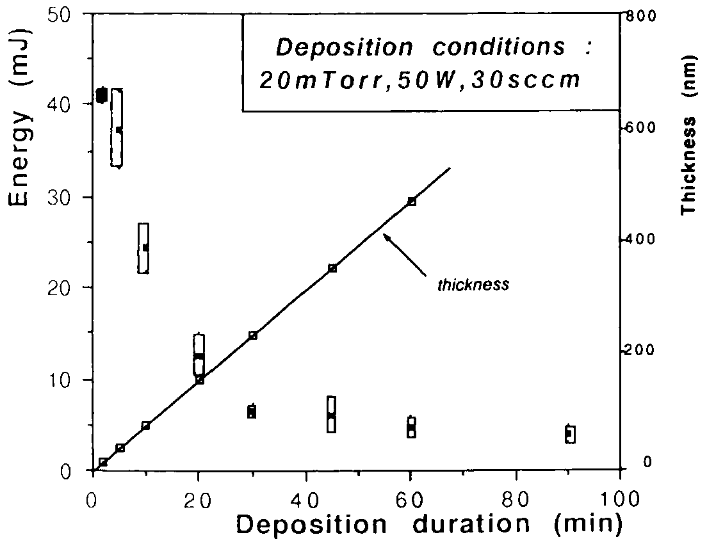


FIGURE 9 Adhesion properties of carbon films elaborated over variable duration.

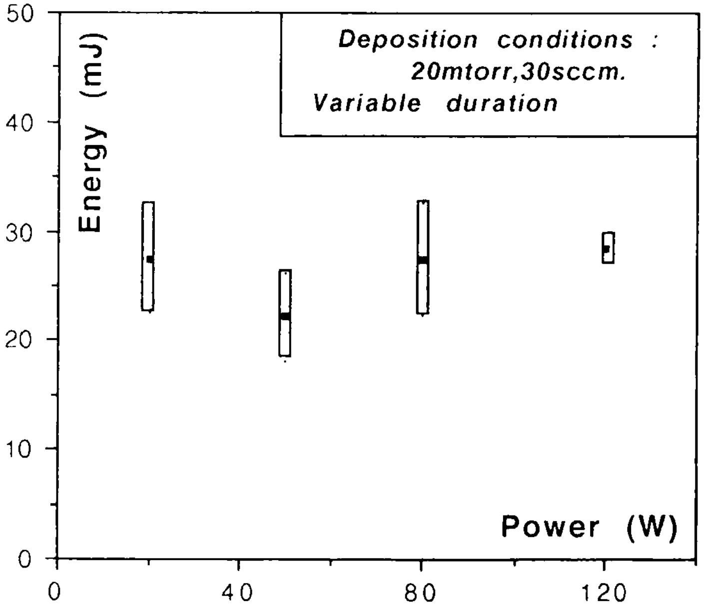


FIGURE 10 Adhesion properties of carbon films of the same thickness (80 nm) elaborated under various power values.

place at the film/adhesive interface. It is to be noted that this delamination is less easy for films deposited at 20 mTorr than for films deposited at 50 mTorr. At the present time, we do not know whether this is due to thickness or structure effects.

Figure 8 shows variation in film adhesion properties when deposition pressure changes. Here too, there is a fall in adhesion performance as pressure increases, therefore as thickness increases. The same trend is observed in Figure 9 which represents variation in film adhesion properties *versus* deposition duration, therefore *versus* thickness. From these results it clearly appears that the lower the thickness, the better the film/substrate adhesion which conforms to the literature data.[20-22] This is confirmed by Figure 10, which shows that adhesion properties remain unchanged for a constant but small thickness (chosen in this example at 80 nm) obtained for various generator power values and durations. However, for thicker films (500 nm), film/substrate adhesion is improved when the elaboration power increases (Figure 11) but it remains lower than for thin films. This is probably due to the fact that, when the power increases, the ion bombardment is stronger, inducing a stress relaxation in the film.[23] Therefore, the main factor which governs good adhesion is the film thickness, which must be low, whatever the experimental parameters used for elaboration are. It is likely that thick films (more than 100 nm) contain stresses which make them fragile, lowering their resistance to deformation. It is interesting to note that, under certain experimental conditions, some films liberate these stresses by "cracking" on exposure to air.

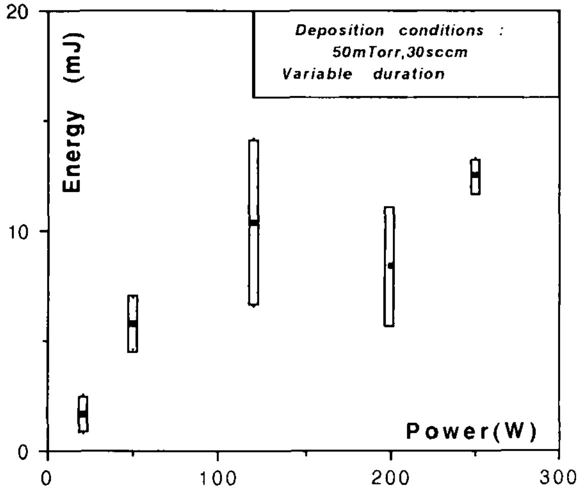


FIGURE 11 Adhesion properties of carbon films of the same thickness (500 nm) elaborated under various power values.

## CONCLUSION

This work shows that it is possible to deposit amorphous hydrogenated carbon films onto stainless steel for adhesion and protection purposes on condition that the surface to be coated has previously been properly treated. For high adhesion to the substrate, these films must be thin (not more than about 80 to 100 nm). In addition, to play the role of adhesion primer, their surfaces must be functionalized to promote chemical bonding with adhesives.

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