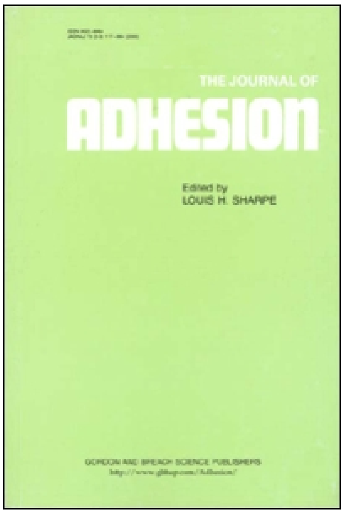

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Molecular Structure of the Interphase Formed by Plasma-Polymerized Acetylene Films and Steel Substrates

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The molecular structure of the interphase between plasma-polymerized acetylene films and steel substrates was determined using in situ reflection–absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS). Plasma-polymerized acetylene films were deposited onto polished steel substrates using argon as a carrier gas and inductively coupled, radio frequency (RF)-powered plasma reactors that were interfaced directly to the XPS and Fourier transform infrared (FTIR) spectrometers. RAIR showed that the plasma polymerized films contained large numbers of methyl and methylene groups but only a small number of mono substituted acetylene groups, indicating that there was substantial rearrangement of the monomer molecules during plasma polymerization. Bands were observed near 1020 and 855 cm^{-1} *in the RAIR spectra that were attributed to skeletal stretching vibrations in C–C–O–Fe groups, indicating that the plasma-polymerized films interacted with the substrate through formation of alkoxide bonds. Another band was observed near 1565 cm*$^{-1}$ *and attributed to carboxylate groups in the interphase between the films and the oxidized surface of the substrate. Results obtained from XPS showed that the surface of the iron substrate consisted mostly of a mixture of* Fe_2O_3 *and FeOOH and that iron was mostly present in the Fe(III) oxidation state. However, during plasma polymerization of acetylene, there was a tendency for the concentration of FeOOH groups to decrease and for the concentration of Fe(II) to increase, due to the reducing nature of argon/acetylene plasmas. Results from XPS also confirmed the formation of alkoxide and carboxylate groups in the interphase during plasma polymerization of acetylene.*

Keywords: Alkoxides; Argon/acetylene plasmas; Carboxylates; Interphase; Plasma etching; Plasma polymerization; Reflection–absorption infrared spectroscopy; X-ray photoelectron spectroscopy

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I. INTRODUCTION

Adhesion of natural rubber to metals is important in many areas, including the tire and automobile industries. However, adhesion of most natural rubber compounds to the oxidized surfaces of metal substrates is poor. An important exception concerns brass substrates; when natural rubber compounds are cross-linked in contact with brass substrates, outstanding adhesion of the rubbers to the substrates is usually observed [1]. Because of the poor adhesion of natural rubber compounds to most metal substrates, surface engineering processes must usually be applied to metal substrates before adhesion of rubber compounds to the substrates can be obtained. Processes such as plating steel substrates with brass or applying specialized primers and adhesives have been used to obtain adhesion of natural rubber compounds to steel substrates. Buchan reviewed early work in this field [1]. More recently, van Ooij and coworkers have reviewed adhesion of rubber to brass-plated steel [2], and Sexsmith [3] has reviewed the use of polymers as adhesives and primers.

Although these surface engineering processes are effective, they still present some problems. Plating processes are sometimes difficult to control and generate liquid wastes that must be disposed of properly. Specialized adhesives and primers frequently involve organic solvents that must be controlled. As a result, there is a need for innovative new surface engineering processes for adhering natural rubber to metal substrates such as steel while the rubber is being cross-linked.

Our research group has been interested in a new process for obtaining adhesion of natural rubber compounds to steel substrates that involves etching or cleaning the substrates in oxygen or argon plasmas, applying plasma-polymerized hydrocarbon films to the substrates as "templates," and then cross-linking the rubber in contact with the film-covered surface of the substrates. Plasma processing is attractive for several reasons. It is an environmentally compatible, gas-phase process that does not result in liquid wastes. Substrates can be cleaned and then coated with a plasma polymer film in the same vacuum chamber, and the process can be carried out on a continuous or semicontinuous basis, especially for substrates such as wires. Plasma processing is also economical; the biggest operating cost is probably associated with running the vacuum pumps. Perhaps the biggest drawback is that most plasma processing is carried out at pressures less than atmospheric pressure, although atmospheric-pressure plasma systems are now available for at least some types of plasma processing [4].

Initially, we considered ethylene, ethane, and acetylene as feed gases or monomers for depositing plasma-polymerized templates for adhering natural rubber compounds to steel substrates [5,6]. Ethylene polymerized readily but formed only oily films, whereas ethane polymerized more slowly and formed solid films over a wide range of reactor parameters. However, films formed from ethane or ethylene were not useful as templates for adhering natural rubber compounds to steel substrates [6].

Plasma polymerization of acetylene resulted in solid films that were highly effective templates for rubber-to-metal bonding [5–7]. Thus, the initial strength of miniature lap joints prepared from steel substrates coated with plasma-polymerized acetylene primer films and then bonded using natural rubber as an adhesive was about 31 MPa, and failure was completely cohesive within the rubber. These results were very similar to those obtained from miniature lap joints that were prepared from brass substrates [7]. The durability of miniature lap joints prepared from polished steel substrates primed with plasma-polymerized acetylene films was also excellent. After exposure to steam at 121°C for 3 days, the strength of the joints decreased slightly, but failure was still cohesive within the adhesive [7].

Considering that plasma polymerization of acetylene is an effective, cost-efficient process for depositing template films onto steel substrates prior to cross-linking natural rubber against the substrates, we have been interested in elucidating the molecular structure of the films as well as the various reactions involved in adhering rubber to metals using the films as templates. We have used surface analysis techniques such as reflection–absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS) to determine the molecular structure of plasma-polymerized acetylene films on steel substrates [8]. Results from RAIR showed that as-deposited films contained substantial numbers of methyl and methylene groups. Because these functional groups were not found in acetylene, it was concluded that considerable dissociation of the monomer took place in the plasma. RAIR also showed that residual free radicals in the as-deposited films reacted with oxygen and water vapor in the atmosphere to form carbonyl and hydroxyl groups. These results were substantiated by XPS, which showed that the concentration of oxygen in as-deposited films was small but increased quickly during exposure to the atmosphere [8].

We have also used RAIR and XPS to investigate reactions that occur between a model rubber compound consisting of a mixture of squalene, zinc oxide, carbon black, sulfur, stearic acid, diaryl-p-diphenylene-amine, and N,N-dicyclohexyl-benzothiazole sulfenamide (DCBS) and plasma-polymerized acetylene films, and we have used the results to develop a model for the reaction of an actual natural rubber compound with the films [9,10]. According to this model, zinc oxide reacted with stearic acid to form zinc stearate, which then reacted with DCBS and sulfur to form an accelerator complex and zinc perthiomercaptides. The perthiomercaptides reacted with squalene and the plasma polymer to form pendant groups that eventually disproportionated to form cross-links between the primer films and squalene [9].

Although the mechanisms responsible for adhesion in the interphase between natural rubber and plasma-polymerized acetylene films are thus reasonably well understood, relatively little is known about the structure of the interphase between the films and the oxidized surfaces of steel substrates. The objective of the research described here was to determine the molecular structure of the film/substrate interphase using *in situ* RAIR and XPS. Using *in situ* techniques in which plasma-polymerized acetylene films were deposited onto polished steel substrates in plasma reactors that were interfaced directly to XPS and Fourier-transform infrared (FTIR) spectrometers, allowed the film/substrate interphase to be probed without complications caused by exposure of the samples to the laboratory atmosphere. *In situ* techniques had an additional benefit in the case of RAIR spectroscopy because they made it possible to obtain spectra of the substrate and the substrate plus film without moving the substrate; this facilitated subtraction of the spectra to get the spectra of the films.

II. EXPERIMENTAL

Cold-rolled steel (CRS) substrates were cut into coupons 1 cm × 1 cm for XPS and 7.62 cm × 2.54 cm for RAIR. The steel coupons were rinsed with acetone, blown dry with nitrogen, and then ground and polished. SiC papers with grits of 600, 800, and 1200 were used to grind the surfaces of the coupons. The substrates were wiped with ethanol and blown dry with nitrogen after each step in the grinding process. Rough polishing was then carried out on a Nylon polishing cloth using diamond paste with particle sizes of 15 and 5 μm. Final polishing was done with microcloth using an aqueous alumina suspension with a particle size of 2 μm.

Polished steel substrates were placed in purpose-built, inductively coupled, RF-powered reactors that were attached directly to the XPS and FTIR spectrometers and then etched in oxygen and argon plasmas before deposition of the plasma-polymerized acetylene films. Plasma etching was carried out at a pressure of 0.1 torr, power of 120 w, and a flow rate of 50 standard cubic centimeters per second (sccm). Plasma polymerization of acetylene was carried out in the same reactors using argon as the carrier gas at a pressure of 0.075 torr, power of 60 w, argon flow rate of 16 sccm, and acetylene flow rate of 20 sccm. The reactors were evacuated with turbomolecular pumps before the plasma-etching and plasma-polymerization processes were started. The use of turbomolecular pumps reduced the oxygen content in the reactors; water adsorbed onto the reactor walls resulted in films with relatively high content of carboxyl and carbonyl functional groups.

The thickness of the plasma-polymerized films was determined using a variable-angle, spectroscopic ellipsometer (VASE) from J. A. Woollam (Lincoln, NE, USA). WVASE 32 software from Woollam was used to calculate the thickness of the films from the changes in the polarization state of the light reflected from the polished surfaces of the samples. A Cauchy model was used to determine the thickness of the plasma-polymerized films.

The roughness of the polished substrates before and after etching in argon plasmas was determined using a Dimension 3100 atomic force microscope with Nanoscope IIIa Controller (Veeco Metrology, Inc., Santa Barbara, CA, USA). The images were collected in tapping mode (silicon probe) using a 1-μm X-axis scale, 1-μm Y-axis scale, and 20-nm Z-axis scale.

As discussed previously, *in situ* RAIR spectra of plasma-polymerized acetylene films were collected using a Nicolet Magna 760 Fourier-transform infrared spectrometer (Thermo Electron Corp., Madison, WI, USA) that was interfaced directly to an inductively coupled, RF-powered reactor. A schematic drawing of the reactor interfaced to the FTIR spectrometer is shown in Figure 1. This reactor, which has been described more completely elsewhere [11], enabled RAIR spectra to be obtained using one reflection of the IR beam from the substrate at an angle of 82° while the sample was kept under vacuum or in an inert environment. All RAIR spectra were collected at a resolution of 4 cm^{-1} using a mercury–cadmium–telluride (MCT) detector. Many scans (4096) were used to collect spectra of the plasma polymer films. All instrument control, data acquisition, and data manipulation were carried out using OMNIC software provided by Thermo Electron.

The exact procedure used to obtain the RAIR spectra was as follows. A freshly polished steel substrate was placed into the plasma reactor and aligned so that the intensity reaching the MCT detector was maximized. The reactor was evacuated to a base pressure of 0.010 torr and then back-filled with argon to a pressure of 0.1 torr. Etching of the substrate was then carried out in an argon plasma using the parameters discussed previously. The reactor was again evacuated to the base

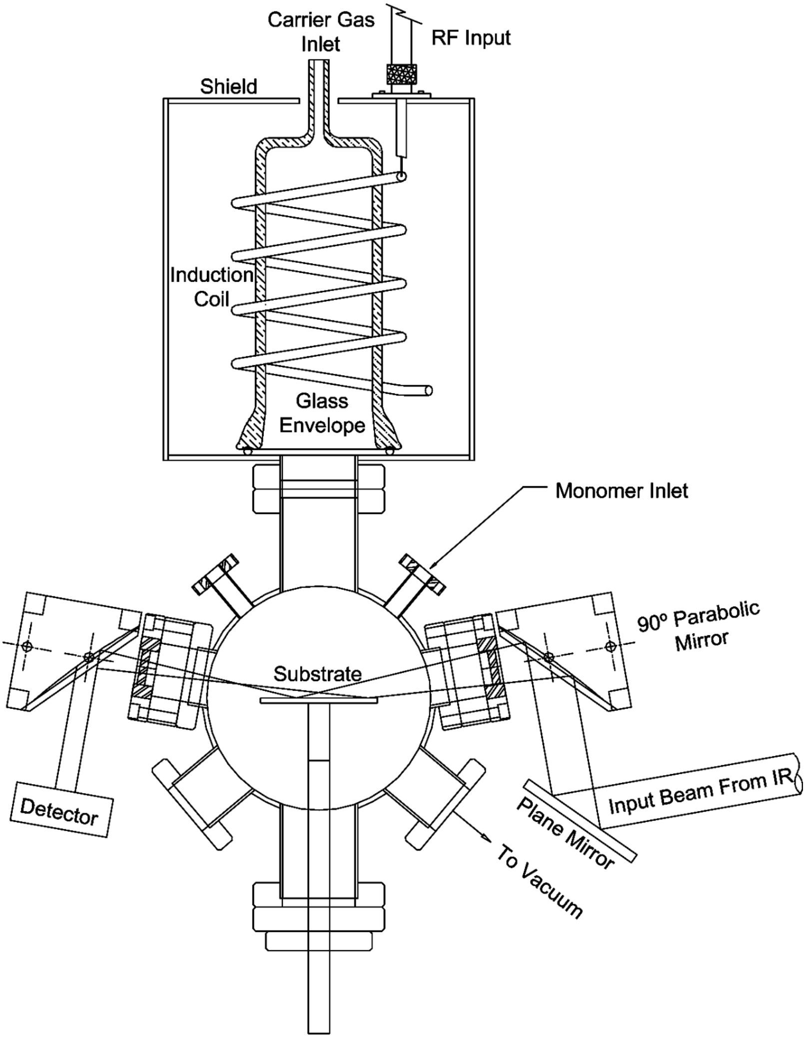

FIGURE 1 Schematic drawing of the *in situ*, RF-powered plasma reactor that was interfaced with the FTIR spectrometer. Copyright 2002, from R. H. Turner and F. J. Boerio, "Molecular Structure of Interfaces Formed with Plasma Polymerized Silica-Like Primer Films, Part I: Characterization of the Primer/Metal Interface using Infrared Spectroscopy *In situ*," *J. Adhesion* **78**, 447–464 (2002). Reproduced by permission of Taylor and Francis Group, LLC, http://www.taylorandfrancis.com.

pressure, and the RAIR spectrum of the etched substrate was obtained. A plasma-polymerized acetylene film was then deposited onto the substrate using the deposition parameters discussed previously. The reactor was again evacuated to the base pressure, and the RAIR spectrum of the substrate plus film was obtained. The RAIR spectrum of the substrate was then subtracted from that of the substrate plus film to get the spectrum of the film.

A similar procedure was used to characterize the steel substrates, and the films formed on them during plasma polymerization by X-ray photoelectron spectroscopy (XPS). CRS substrates were etched and/or coated with plasma-polymerized acetylene films in an inductively coupled, RF-powered reactor that was interfaced with a Perkin-Elmer model 5300 XPS spectrometer (Perkin-Elmer, Eden Prairie, MN, USA). In this system, substrates were etched and/or coated with plasma-polymerized films in the plasma reactor and then inserted into the analysis chamber of the XPS spectrometer for analysis without being exposed to the laboratory environment. However, a connecting vacuum chamber was located between the analysis chamber and the plasma reactor and maintained at intermediate vacuum levels so that samples could be transferred from the relatively high pressure of the plasma reactor to the relatively low pressure of the analysis chamber without degrading the vacuum in the analysis chamber.

A schematic drawing of the reactor system interfaced to the XPS spectrometer is shown in Figure 2. This reactor has also been described more completely elsewhere [12]. XPS spectra were excited using Mg Kα radiation (1253.6 eV). Survey spectra were collected with the pass energy set to 89.45 eV and with a step size of 0.5 eV. High-resolution spectra were obtained using a pass energy of 35.75 eV and 0.05 eV/step. All of the spectra presented here were obtained using a takeoff angle of 45°. The effects of sample charging were eliminated by referring the C(1s) binding energy of adventitious carbon to a value of 284.6 eV. XPS instrument control, data acquisition, and data processing were carried out using AugerScan-2 software (RBD Enterprises, Bend, OR, USA). The pressure inside the XPS analysis chamber was typically about 1×10^{-9} torr while spectra were being obtained.

The exact procedure used to obtain the XPS spectra was as follows. A polished CRS substrate was loaded into the plasma reactor that was interfaced to the XPS spectrometer, and the reactor was evacuated to a base pressure of about 0.010 torr. The substrate was then etched in an argon plasma using the parameters shown in Table 1. After etching was completed, the substrate was transferred from the plasma reactor to the connecting vacuum chamber, which was pumped down to a base

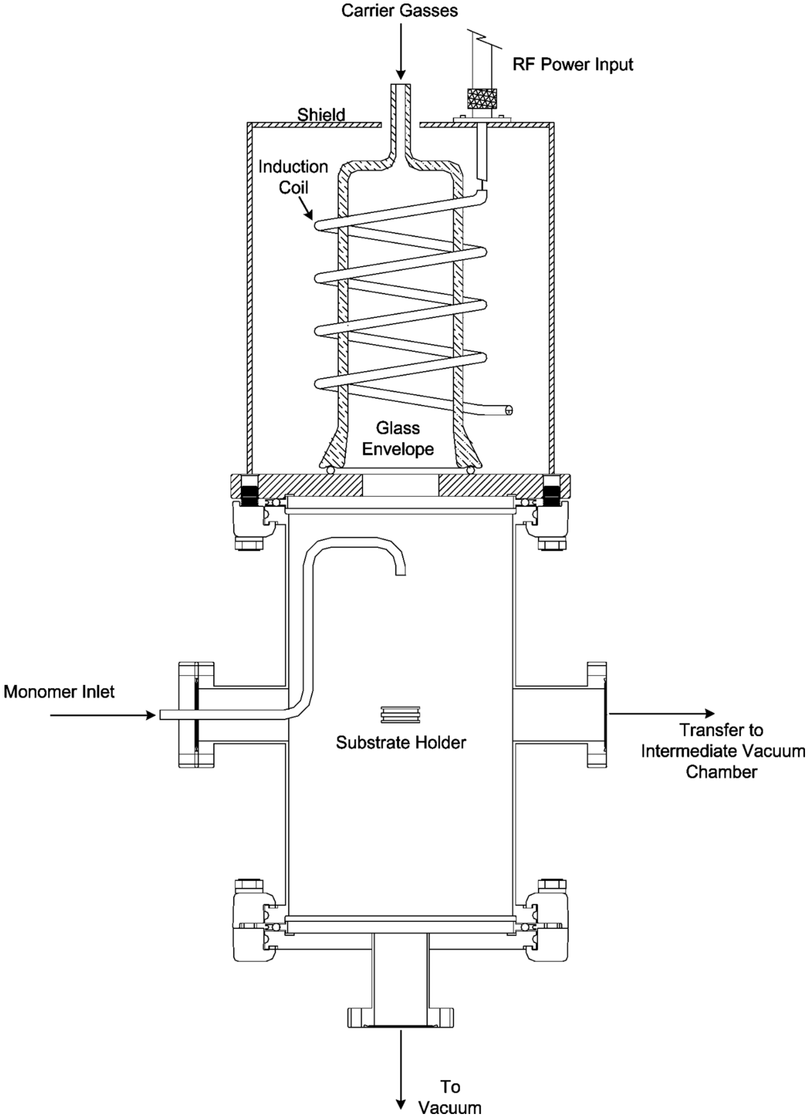

FIGURE 2 Schematic drawing of the *in situ*, RF-powered plasma reactor that was interfaced with the XPS spectrometer. Copyright 2002, from R. H. Turner and F. J. Boerio, "Molecular Structure of Interfaces Formed with Plasma Polymerized Silica-Like Primer Films, Part I: Characterization of the Primer/Metal Interface using X-ray Photoelectron Spectroscopy *In situ*," *J. Adhesion* **78**, 465–493 (2002). Reproduced by permission of Taylor and Francis Group, LLC, http://www.taylorandfrancis.com.

TABLE 1 Process Parameters Used during Etching of Polished Cold-Rolled Steel Substrates in RF Plasmas

Etching gas	Pressure (torr)	Power (watts)	Flow rate (sccm)
Oxygen	0.1	120	50
Argon	0.1	120	50

pressure between 10^{-8} and 10^{-9} torr. When the pressure in the connecting chamber reached the base pressure, a gate valve separating the connecting and analysis chambers was opened, and the sample was inserted into the analysis chamber of the XPS spectrometer. The gate valve was then closed, and the XPS spectrum of the substrate was obtained. After the spectrum of the substrate was obtained, the gate valve was opened, and the substrate was withdrawn back into the connecting chamber. From there, the substrate was inserted back into the plasma reactor, and a plasma-polymerized acetylene film was deposited using the parameters shown in Table 1. The substrate was then removed from the reactor and reinserted into the XPS analysis chamber so that the XPS spectrum of the plasma polymer film could be obtained.

Fe(II) acetate was obtained from Aldrich (Milwaukee, WI, USA) and was used as received. Samples were prepared for XPS by pressing the powdered material into double-sided adhesive tape, which was supported by a stainless steel sample holder.

III. RESULTS AND DISCUSSION

In Situ RAIR Spectroscopy of Plasma-Polymerized Acetylene Films on CRS Substrates

Plasma-polymerized acetylene films were deposited onto polished steel substrates using an RF-powered, inductively coupled reactor interfaced with the FTIR spectrometer. It was considered that the RAIR spectra obtained from films deposited for relatively long times would be characteristic of the bulk of the films, whereas RAIR spectra of films deposited for relatively short times would be characteristic of the film/substrate interphase. Therefore, deposition times of 60, 45, 30, and 20 s were considered, resulting in plasma polymer films having thicknesses of 382, 171, 62, and 41 Å, respectively.

The *in situ* RAIR spectrum for a film deposited for 60 s and having a thickness of approximately 382 Å is shown in Figure 3. The most

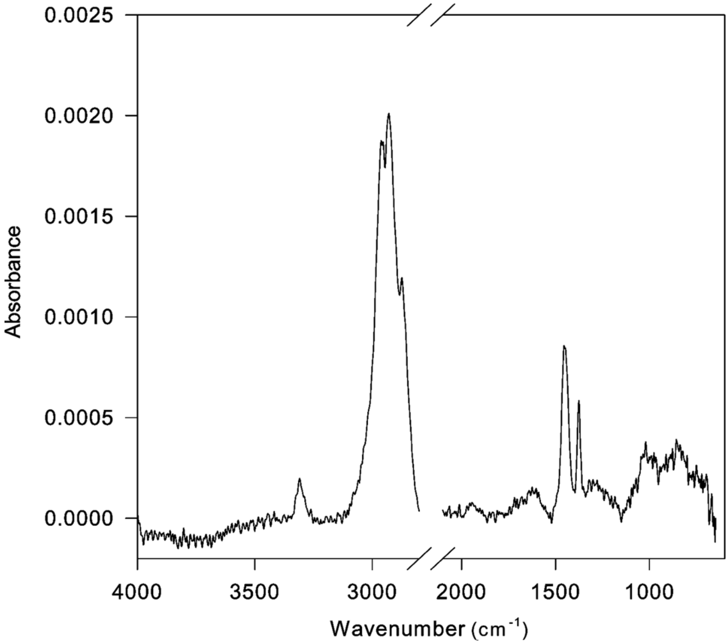

FIGURE 3 RAIR spectrum obtained from a film that was deposited onto a polished cold-rolled steel substrate by plasma polymerization of acetylene in the *in situ* RF-powered reactor for 60 s. The substrate was etched in oxygen and argon plasmas before deposition of the film.

intense absorption bands in the RAIR spectrum were near 2960, 2932, and 2871 cm^{-1} and were assigned to asymmetric CH_3 stretching, CH_2 stretching, and CH_3 symmetric stretching modes, respectively. Absorption bands with medium intensity were also observed near 1450 and 1375 cm^{-1} and assigned to CH_2 and CH_3 bending modes, respectively. A weak absorption band assigned to CH stretching in monosubstituted acetylene groups was located near 3305 cm^{-1}.

The presence of strong bands related to methyl and methylene groups and the relative weakness of the band due to CH stretching in monosubstituted acetylene groups indicated that there was considerable fragmentation and rearrangement of the acetylene monomer in the RF plasma. We have previously observed strong bands near 1700 cm^{-1} in RAIR spectra of films that were exposed to the laboratory environment [8]. These bands were assigned to carbonyl groups that resulted from the reaction of residual free radicals in the plasma-polymerized acetylene films with oxygen and water vapor during exposure to the laboratory atmosphere. However, reference to Figure 3 indicates that a weak absorption band characteristic of carbonyl groups was observed near 1700 cm^{-1} in RAIR spectra of plasma-polymerized acetylene films deposited on steel substrates in the *in situ* reactor for 60 s. There was evidently enough water vapor and oxygen available inside the *in situ* reactor to form a relatively low concentration of oxygen-containing functional groups. A weak band was also observed near 1648 cm^{-1} in the spectrum of the film formed in 60 s (see Figure 3) and was related to the $>C{=}C<$ stretching mode of vinyl or vinylidene groups.

As indicated previously, a deposition time of 60 s resulted in films that were approximately 382 Å in thickness; this thickness was too great for any bands characteristic of the film/substrate interphase to be revealed. Therefore, the deposition time was reduced to 30 s, resulting in a film having a thickness of about 62 Å; the RAIR spectrum obtained from this film is shown in Figure 4. When the spectrum

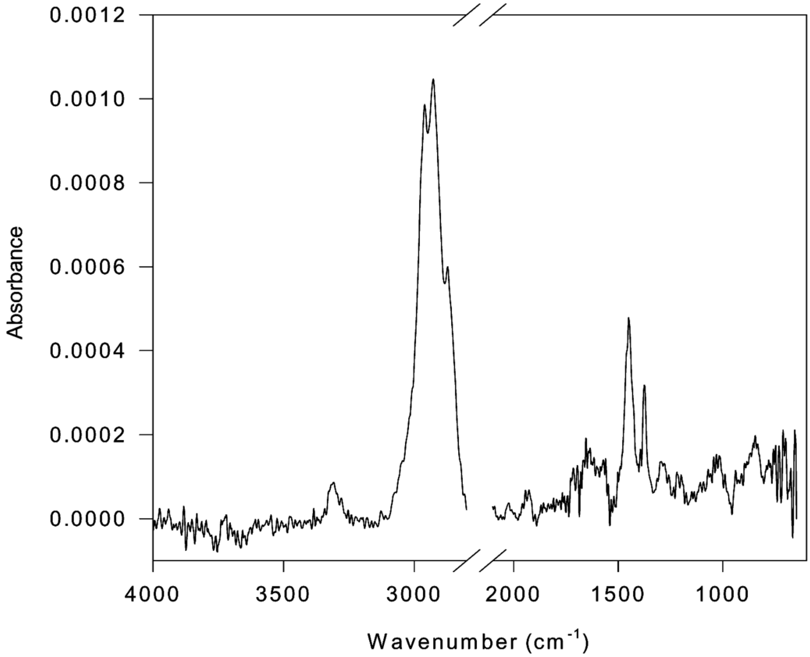

FIGURE 4 RAIR spectrum obtained from a film that was deposited onto a polished cold-rolled steel substrate by plasma polymerization of acetylene in the *in situ* RF-powered reactor for 30 s. The substrate was etched in oxygen and argon plasmas before deposition of the film.

in Figure 4 was compared with that shown in Figure 3, it was noted that the intensity of most of the bands in the spectrum had decreased by a factor of approximately two, as expected. Thus, the band at 2932 and 1450 cm^{-1} decreased in intensity from about 0.0021 and 0.0010 absorption units, respectively, for the film deposited during 60 s to approximately 0.0011 and 0.0005 units, respectively, for the film deposited during 30 s. However, new, weak bands that were possibly related to the film/substrate interphase were observed near 1565, 1014, and 856 cm^{-1}.

The deposition time was decreased again, to 15 s, in an effort to accentuate absorption bands related to the interphase between the plasma-polymerized acetylene film and the polished steel substrate. The RAIR spectrum of this film, which had a thickness of about 49 Å, is shown in Figure 5. As expected, most of the bands in the spectrum decreased in intensity again. However, the intensity of the bands

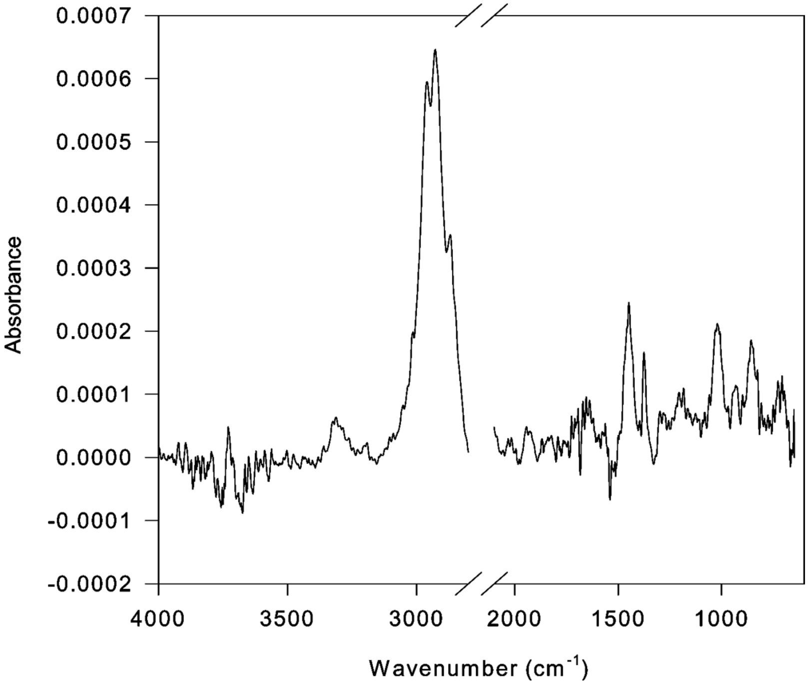

FIGURE 5 RAIR spectrum obtained from a film that was deposited onto a polished cold-rolled steel substrate by plasma polymerization of acetylene in the *in situ* RF-powered reactor for 15 s. The substrate was etched in oxygen and argon plasmas before deposition of the film.

near 1565, 1014, and 856 cm^{-1} stayed approximately constant, indicating that these bands were related to the interphase rather than to the bulk of the films.

Blyholder and Neff assigned strong bands near 1050 and 880 cm^{-1} to C–O or skeletal stretching vibrations in alkoxide compounds formed by alcohols such as methanol, ethanol, and propanol adsorbed onto iron. The M–O stretching vibration was located at much lower frequencies, near 500 cm^{-1}, and had low intensity [13]. Poling made a similar assignment for an absorption band in the 1010–1100 cm^{-1} region of acetylenic films formed on iron and steel mirrors [14]. Based on the results of Blyholder and Neff and Poling, we have assigned the bands near 1014 and 856 cm^{-1} in the RAIR spectra of plasma-polymerized acetylene films formed on polished steel substrates to skeletal stretching modes of alkoxides formed at the film/substrate interphase. The band near 1565 cm^{-1} was assigned to a stretching mode of carboxyl groups that were also formed at the film/substrate interphase. To our best knowledge, this is the first time that the formation of specific bonds has been observed at the interphase between plasma-polymerized films and the substrates on which they were deposited.

In Situ XPS Characterization of Plasma-Polymerized Acetylene Films on CRS Substrates

The structure of the interphase between plasma-polymerized acetylene films and steel substrates was also determined using the *in situ* XPS technique and an inductively coupled, RF-powered reactor interfaced directly to the XPS spectrometer. Deposition times of 45, 30, 25, 15, and 10 s were considered. The chemical composition of the resulting films as determined by XPS is summarized in Table 2. Reference to

TABLE 2 Chemical Composition as a Function of Deposition Time for Plasma-Polymerized Acetylene Films Deposited onto Polished Cold-Rolled Steel Substrates (Substrates were Etched in Oxygen and Argon Plasmas before Deposition of the Films)

Deposition time (s)	C (%)	O (%)	N (%)	Fe (%)	S (%)	Zn (%)
0	8.4	63.3	0.3	24.3	2.4	1.3
10	3.4	66.1	0.5	25.9	3.5	0.5
15	38.1	48.0	0.8	11.3	1.9	–
25	45.6	43.0	1.0	8.4	2.0	–
30	53.2	39.0	0.3	5.8	1.8	–
45	97.2	2.6	0.2	–	–	–

Table 2 indicates that there was an induction time of approximately 10 s during which little if any film formation occurred. During this time, the concentration of carbon on the surface actually decreased from about 8.4% to about 3.4% while the concentrations of oxygen and iron increased slightly, from 63.3 to 66.1% and from 24.3 to 25.9%, respectively. Increased surface roughness due to plasma etching of the substrates could cause apparent changes in surface composition. However, the substrates were mechanically polished and had a root mean square (RMS) roughness of about 2.5 nm as determined by atomic force microscopy; changes in surface roughness due to plasma etching were insignificant when compared with roughness features introduced by polishing. The decrease in carbon concentration during the first few seconds of deposition was related to etching or cleaning of the surface by bombardment with argon ions. Following the induction time, formation of a hydrocarbon film occurred rapidly, burying the oxide and the interphase. As a result, the concentration of carbon on the surface increased from 8.4 to 97.2% after 45 s while that of oxygen decreased from 63.3 to 2.6%; no iron was detected after 45 s. Deposition times of 45, 30, 25, and 15 s resulted in plasma-polymerized acetylene films having thicknesses of 171, 83, 64, and 49 Å, respectively.

The XPS survey spectra of plasma-polymerized acetylene films deposited on polished CRS substrates for 45, 30, 25, and 15 s are shown in Figure 6. For relatively long deposition times and thick films, the survey spectra were dominated by a strong peak at 284.6 eV that was related to carbon and by a much weaker peak at 530.0 eV that was related to oxygen. No peaks that were characteristic of the substrate were observed in the survey spectra. When the deposition time was reduced to 30 or 25 s, the peak due to carbon decreased in intensity while that due to oxygen increased. Several peaks related to iron also appeared between about 700 and 750 eV. When the deposition time was reduced to 15 s, the peaks due to oxygen and iron again increased in intensity while that due to carbon decreased. It was evident that for relatively long deposition times, peaks due to the plasma-polymerized acetylene films dominated the survey spectra but for short deposition times, peaks related to the substrate dominated the spectra.

The high-resolution C(1s) spectra obtained from films deposited on polished CRS substrates for 45, 30, 25, and 15 s are shown in Figure 7. For relatively long deposition times such as 45 s, the C(1s) spectra consisted of a strong component near 284.6 eV that was assigned to $\underline{C}$–C and $\underline{C}$–H bonds, a much weaker component near 286.0 eV that was attributed to $\underline{C}$–O bonds, and a very weak component near 287.3 eV

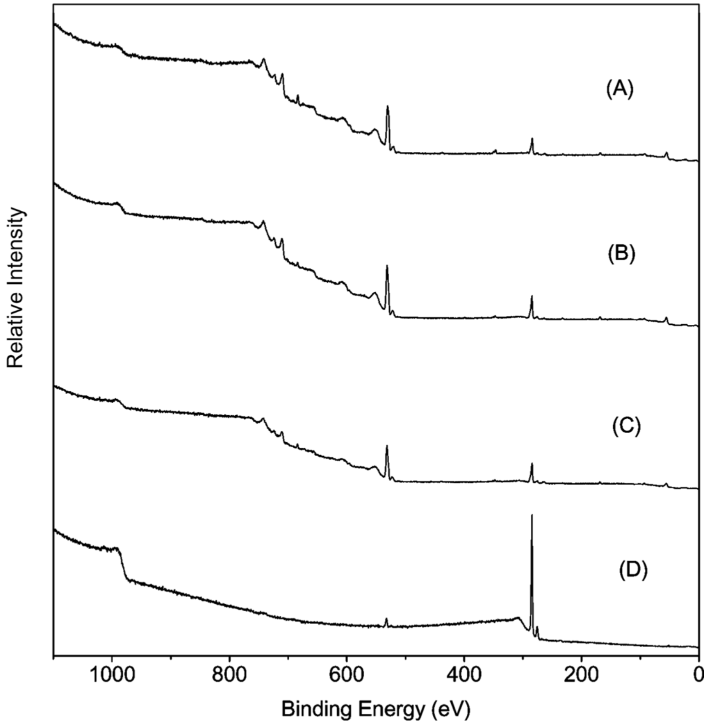

FIGURE 6 XPS survey spectra obtained from plasma-polymerized acetylene films deposited onto polished cold-rolled steel substrates for (A) 15, (B) 25, (C) 30, and (D) 45 seconds using the *in situ* RF-powered reactor. The polished cold-rolled steel substrates were etched in argon plasmas for 10 min prior to deposition of the films.

that was attributed to $>\underline{C}{=}O$ bonds. The C(1s) spectra of the films deposited for shorter times were much more complex and obviously contained additional components. Initially, these spectra were fitted with the same three components located near 284.6, 286.0, and 287.3 eV, plus a fourth component related to $-\underline{C}(O)-O$ bonds that was located at 288.8 eV. However, a good fit of the C(1s) spectra of films deposited at 30, 25, and 15 s could not be obtained using only these four components. To obtain a good fit of the C(1s) spectra, it was necessary to add two additional components, at 287.0 and 288.4 eV. The component at 288.4 eV was shifted upward in binding energy by 3.8 eV from the main component of the C(1s) spectra and was assigned to carbon in carboxylate groups in the film/substrate interphase. Assignment of the component near 288.4 eV in the C(1s)

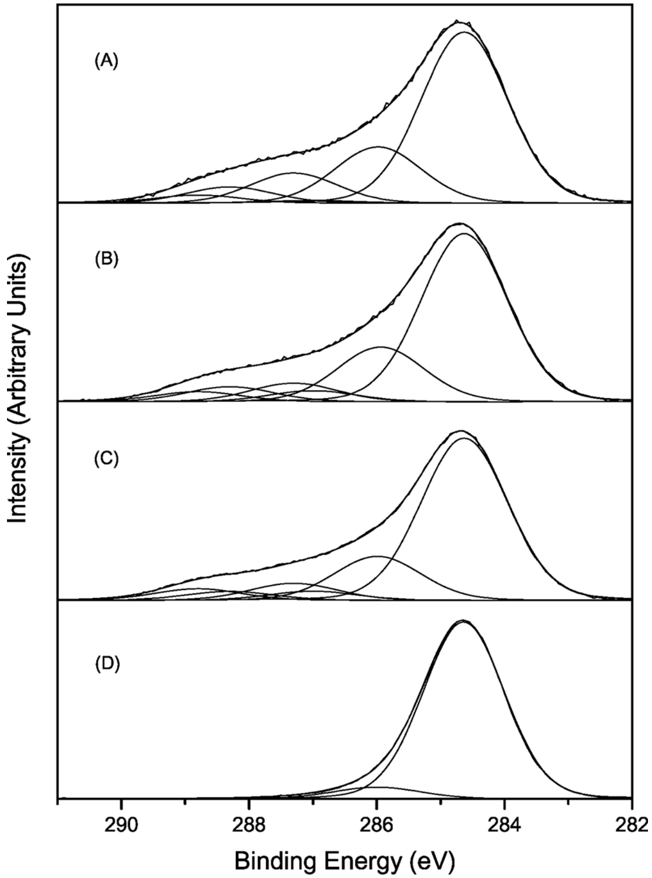

FIGURE 7 High-resolution C(1s) XPS spectra obtained from plasma-polymerized acetylene films deposited onto polished cold-rolled steel substrates for (A) 15, (B) 25, (C) 30, and (D) 45 s using the *in situ* RF-powered reactor. The polished cold-rolled steel substrates were etched in argon plasmas for 10 min prior to deposition of the films.

spectra of plasma-polymerized acetylene films on steel to carboxylate groups was substantiated by the C(1s) XPS spectra of Fe(II) acetate, which consisted of components near 284.6 and 288.4 eV that were obviously related to $\underline{C}$—C/$\underline{C}$—H bonds and to carbon in carboxylate groups, respectively. The component at 287.0 eV in the C(1s) spectra of plasma-polymerized acetylene films on steel was assigned to carbon atoms in alkoxide groups in the interphase. Although no references to XPS spectra of iron alkoxides were found, several groups have

TABLE 3 Band Assignments in the High-Resolution C(1s) XPS Spectra of Plasma-Polymerized Acetylene Films Deposited onto Polished Cold-Rolled Steel Substrates for Various Times

Deposition time (s)	284.6 eV (%)	286.0 eV (%)	287.0 eV (%)	287.3 eV (%)	288.4 eV (%)	288.8 eV (%)
15	59.4	20.1	4.1	7.1	7.2	2.1
25	61.0	19.5	3.9	6.4	6.2	3.0
30	64.2	17.7	3.5	6.3	4.2	4.1
45	92.5	7.1	–	0.4	–	–

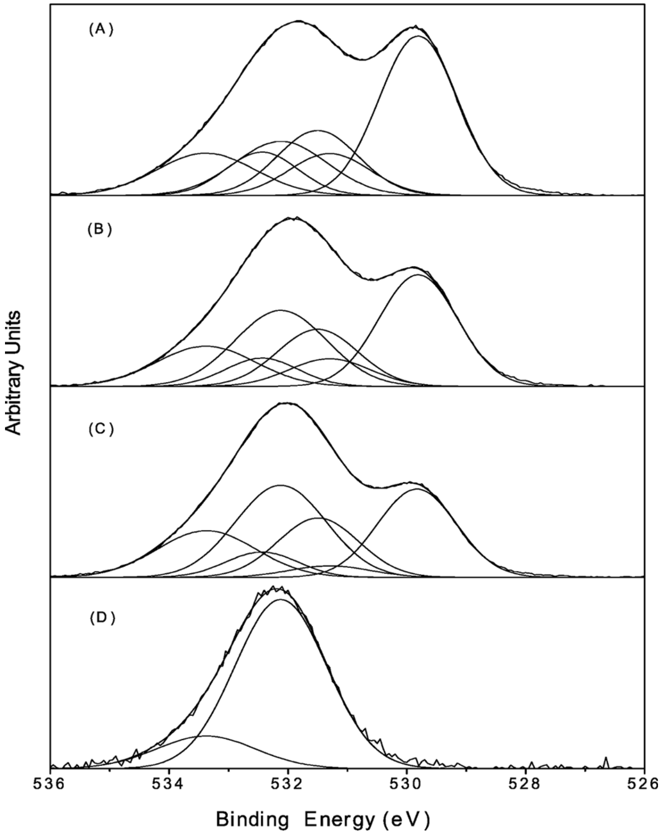

FIGURE 8 High-resolution O(1s) XPS spectra obtained from plasma-polymerized acetylene films deposited onto polished cold-rolled steel substrates for (A) 15, (B) 25, (C) 30, and (D) 45 s using the *in situ* RF-powered reactor. The polished cold-rolled steel substrates were etched in argon plasmas for 10 min prior to deposition of the films.

reported XPS spectra of other metal alkoxides. For example, Lloyd *et al.* reported XPS spectra of methoxides formed by adsorption of methanol onto UO_2 surfaces [15]. They found that the C(1s) binding energy of the methoxide was 287.4 eV. Farfan-Arribas and Madix investigated the adsorption of ethanol onto TiO_2 surfaces and reported that the C(1s) binding energy for the ethoxide was 286.6 eV [16]. Therefore, the assignment of the component at 287.0 eV in the XPS spectra of plasma-polymerized acetylene films on steel substrates to an alkoxide in the interphase seemed reasonable. A summary of the curve-fitted C(1s) spectra of the films deposited on steel substrates for 45, 30, 25, and 15 s is shown in Table 3.

The high-resolution O(1s) spectra obtained from films deposited during times of 45, 30, 25, and 15 s are shown in Figure 8. For a deposition time of 15 s, two maxima were observed in the O(1s) envelope, at 529.8 and 531.8 eV; the maximum at 529.8 eV did not change in position as deposition time increased, but the maximum at 531.8 eV shifted toward higher binding energies and was located at 532.2 eV for films deposited during 45 s. The O(1s) spectra obviously consisted of several components that were characteristic of the substrate surface, the film/substrate interphase, and the bulk of the films and were fitted with a total of six components (see Table 4). The spectrum of the film formed during a deposition time of 45 s was relatively simple and was fitted with two components, one at 532.1 and the other at 533.4 eV that were assigned to $C{=}\underline{O}$ and to $\underline{C}{-}O$ groups in the plasma-polymerized films, respectively. Because no components due to the oxide were observed, it was concluded that the films formed during 45 s were continuous and that the thickness of these films was consistent with the value determined by ellipsometry (*i.e.*, 171 Å). The high-resolution O(1s) XPS spectra of films deposited for deposition times of 30, 25, and

TABLE 4 Band Assignments in the High-Resolution O(1s) XPS Spectra of Plasma-Polymerized Acetylene Films Deposited onto Polished Cold-Rolled Steel Substrates for Various Deposition Times (the Substrates were Etched in Oxygen and Argon Plasmas before the Deposition of the Films)

Deposition time (s)	529.8 eV O^{2-} (%)	531.3 eV carboxylate (%)	531.5 eV OH^- (%)	532.1 eV $C{=}\underline{O}$ (%)	532.4 eV alkoxide (%)	533.4 eV $C{-}\underline{O}$ (%)
15	37.4	10.1	15.7	14.9	9.4	12.5
25	30.7	7.8	16.1	24.4	7.1	13.8
30	25.4	3.4	17.5	29.8	7.6	16.3
45	–	–	–	82.9	–	17.1

15 s were much more complex (see Figure 8 and Table 4) and included components at 529.8, 531.3, and 531.5, and 532.4 eV as well as the components at 532.1 and 533.4 eV. Components at 529.8 and 531.5 eV were attributed to oxygen in the substrate oxide and hydroxide, respectively. The components at 531.3 and 532.4 eV were attributed to O(1s) electrons in carboxylate and alkoxide groups, respectively. We found that the O(1s) binding energy for the carboxylate groups in Fe(II) acetate was also 531.3 eV. Most investigators that have considered the XPS spectra of alkoxides have not reported the O(1s) binding energy [17]. However, Lloyd *et al.* reported a similar value, 532.2 eV, for the methoxide formed by adsorption of methanol on UO_2 [15]. Therefore, the assignment of the component at 532.4 eV to an iron alkoxide seemed reasonable.

Peaks due to Fe(2p) electrons were observed in XPS spectra for films deposited during 15, 25, and 30 s but not in spectra of films

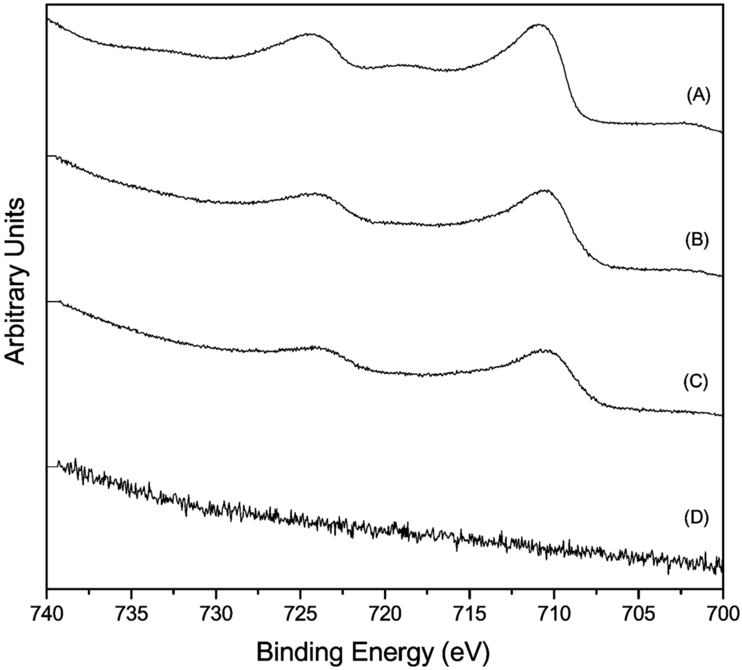

FIGURE 9 Fe(2p) XPS spectra obtained from plasma-polymerized acetylene films deposited onto polished cold-rolled steel substrates for (A) 15, (B) 25, (C) 30, and (D) 45 s using the *in situ* RF-powered reactor. The polished cold-rolled steel substrates were etched in argon plasmas for 10 min prior to deposition of the films.

deposited during 45 s (see Figure 9). The Fe(2p) spectra decreased in intensity significantly as the deposition time and thus the film thickness increased. However, some important changes in the Fe(2p) spectra were observed as the deposition time increased. The Fe(2p$_{3/2}$) peak, which was located at about 711.2 eV for the shortest deposition times, developed a tail toward the low binding energy side, and the position of the maximum in the Fe(2p$_{3/2}$) spectrum moved approximately 0.8 eV toward lower binding energies as deposition time increased. These changes in the Fe(2p) spectra as a function of deposition time were related to the large concentration of hydrogen radicals present in acetylene/argon plasmas and to the reducing nature of such plasmas. As a result, there was some tendency for Fe(III) to be reduced to Fe(II) during exposure of steel substrates to argon/acetylene plasmas. This conclusion was supported by the observation that the Fe satellite at about 718.7 eV for the shortest deposition times shifted toward lower binding energies with increasing deposition time and became part of the tail on the high-binding-energy side of the Fe(2p$_{3/2}$) peak; this shift was also consistent with the tendency of Fe(III) to be reduced Fe(II) [18].

IV. CONCLUSIONS

In situ FTIR and XPS showed that plasma-polymerization of acetylene onto steel substrates in inductively coupled, RF-powered plasma reactors using argon as the carrier gas resulted in the formation of films that interacted with the steel substrates through the formation of alkoxide and carboxylate functional groups. *In situ* FTIR and XPS also showed that the films contained significant numbers of methyl and methylene groups but relatively few monosubstituted acetylene groups. The relative lack of monosubstituted acetylene groups in these films compared with those deposited in a microwave-powered reactor, which contain significant numbers of monosubstituted acetylene groups, was related to ion bombardment of the growing films in the RF reactors. The as-deposited films contained some oxygen-containing functional groups such as carbonyl groups, even though the films were not exposed to oxygen and water vapor in the atmosphere; oxygen-containing functional groups probably formed through reactions with residual water vapor and oxygen adsorbed on the walls of the reactor. However, the concentration of oxygen-containing functional groups was much lower than in films that were exposed to the atmosphere, indicating that residual free radicals in the films reacted with oxygen and water vapor in the atmosphere to produce functional groups such as carbonyl and hydroxyl groups. Acetylene/argon plasmas were reducing in nature because of the large number of hydrogen radicals formed in such plasmas, and there was some tendency for Fe(III) to be reduced to Fe(II) during plasma polymerization of acetylene on steel substrates.

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