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FT-IR and Temperature-programmed Desorption (TPD) Study of the Adsorption of Probe Molecules Used to Model Epoxy Resin Adhesion to Chromium, Iron and Stainless Steel Substrates

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FT-IR and Temperature-programmed Desorption (TPD) Study of the Adsorption of Probe Molecules Used to Model Epoxy Resin Adhesion to Chromium, Iron and Stainless Steel Substrates*

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In this study, we investigated the reactivity of chromium, iron, and surface-treated 304L stainless steels (SS) toward molecules representing model epoxy resins. These molecules were ammonia (a basic probe molecule also representative of the hardener amine group), 1,2-epoxybutane (for epoxy groups) and 2(methylamino)ethanol (for the β -amino alcohol resulting from the reaction of epoxy with amine). These molecules were analyzed in the adsorbed state by either FT-IR or temperature-programmed desorption (TPD).

Surface analysis showed that the top surface of the treated 304L samples only contains chromium and iron as metallic elements. The chromium/iron ratio can be varied within a wide range according to the SS surface treatment used. When increasing the SS surface chromium enrichment, we show a simultaneous increase of (i) both density and strength of surface acid sites, (ii) the amount of β -amino alcohol adsorbed. In addition, there is a marked improvement of the epoxy resin/304L bond strength when the SS surface is more chromium-enriched.

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Keywords: Adhesion; acid-base properties; probe molecules; epoxy adhesives; stainless steel; chromium; iron; XPS; ISS; FT-IR; TPD

INTRODUCTION

Various theories have been proposed [1–4] to explain adhesion mechanisms between organic adhesives and smooth metallic surfaces. The most generally considered model, referred to as the “chemical bond theory” [5], involves the formation of ionic-covalent bonds between some chemical functions of the adhesive and some active sites of an oxidised metal surface (metal cations, oxygen anions, hydroxyl groups...). In order to achieve a durable structural adhesion, the formation of such strong bonds is necessary and that depends largely upon the surface treatment of the substrate.

With this approach to adhesion phenomena, it is interesting to identify and enumerate the active sites and, then, to determine their reactivity toward a specific molecule. Unfortunately, fully-formulated adhesives are generally mixtures of large and complex molecules, and of some fillers. As such mixtures are quite difficult to handle and to analyze, the use of model or probe molecules was considered for fundamental research purposes [6]. These molecules must be representative of some active functions of the adhesive and also possess a well-established chemical behavior, with respect to their acid-base properties, for example.

Epoxy resins and amine-based hardeners are widely used for structural bonding purposes. Adhesives of this family mainly contain some basic reactive functions such as epoxy rings and amine functions which produce amino-alcohol species [7, 8] during adhesive polymerization. All these functions are likely to interact strongly with the acid sites possibly present at the surface of the metallic substrates. These sites can be revealed by ammonia (or pyridine) adsorption and analysis by FT-IR, XPS, SIMS or TPD, *etc.*, as extensively used in catalysis to determine the nature (Lewis or Brønsted), the density, and the strength of acid sites at the surface of many solids [9]. A second step of this work is more specific to adhesion studies as it involves the adsorption of model resin fragments. As proposed by Somorjai *et al.* [10, 11], Affrossman *et al.* [12, 13] and Barthès-Labrousse *et al.* [14], aromatic or aliphatic epoxies and amino-alcohols are suitable model

TABLE I Surface treatments of AISI 304L samples

<i>Treatment</i>	<i>Duration (s)</i>
Ultrasonic cleaning in ethanol	300
Chemical etching in 15% HNO ₃ , 5% HF solution. Temperature: 25°C	300
Plasma oxidizing (13.56 MHz RF power supply) Power density: 0.53 W cm ⁻² Oxygen pressure: 100 mTorr Flow rate: 100 sccm	5 - 300
Anodizing in 65% HNO ₃ solution Temperature: 25°C Current density: 0.5 mA cm ⁻²	60 - 3600
Anodizing in concentrated H ₂ SO ₄ - K ₂ Cr ₂ O ₇ solution Temperature: 70°C Current density: 1.0 mA cm ⁻²	900

Among these treatments, the oxygen-plasma is known to be efficient for contaminant removal [18] and the electrochemical anodizing to promote strong and durable bonds between epoxy resins and SS surfaces [16].

Pure chromium and iron samples used as references were purchased from Goodfellow (UK), mechanically polished with 1 µm diamond paste, cleaned in an ethanol ultrasonic bath, and then treated by short duration (10 s) oxygen-plasma.

XPS and ISS Analyses

XPS and ISS spectra were recorded using a RIBER SIA 200 multi-technique (XPS, AES, ISS) spectrometer, equipped with a MAC 2 analyzer. For XPS, the photoelectrons were detected at a take-off angle of 30° with respect to the sample surface. Non-monochromatized Mg K α radiation was used and the maximum of the C1s peak envelope corresponding to C—C or C—H bonds was assumed to be at a binding energy of 284.6 eV.

The quantitative approach was carried out by measuring the area of Cr 2p and Fe 2p peaks after background correction according to the Shirley method [19]. These values were corrected by means of Scofield coefficients [20], inelastic-mean-free-path of electrons (considered as proportional to the square root of their kinetic energy),

take-off angle, and transmission function of the analyzer. This last parameter was calculated from the equation proposed by Darque-Ceretti *et al.* [21].

For ISS analysis, samples were bombarded with 2 keV Ne^+ ions. Working pressure was 3×10^{-6} Torr and the analyzed area about 3 mm in diameter. After scattering, the ions were detected at a scattering angle of 125° and the take-off angle was 55° with respect to the sample surface.

FT-IR Analysis

FT-IR spectra were obtained using a NICOLET 710 spectrometer monitored by a RISC workstation. This instrument was fitted with a liquid-nitrogen cooled MCT detector, and a SPECAC variable-angle reflection accessory. An incidence angle of 86° was chosen and the infrared radiation was polarized in the p-mode by means of a SPECAC ZnSe grid transmission polarizer. Generally 1024 scans at a resolution of 4 cm^{-1} were co-added to obtain a spectrum. Background was collected on each sample prior to adsorption of 2(methylamino)ethanol. Adsorption was carried out at 80°C for 30 min, followed by a 2 h evacuation at 1×10^{-5} Torr.

TPD Analysis

Metal plates previously described were heated by induction (1.1 MHz) with a six-turn coil surrounding the reactor, connected to either a vacuum line or to a gas line allowing the adsorbate to be introduced. Gas analysis was performed by a mass spectrometer (quadrupole-type RIBER QS100) connected to the reactor. A peak selector allowed four masses to be monitored simultaneously. Recording the complete mass spectrum in the range 1–100 amu was also possible. The TPD apparatus has been described in details elsewhere [22].

Gaseous 1,2-epoxybutane was obtained by evaporation of the liquid (vapor pressure: 310 Torr at 25°C) into the gas line previously evacuated. The experimental mass spectrum shown in Figure 1 is different from the reference data of Cornu and Massot [23]. The additional peaks at 16, 17, 18, 28, 32 and 44 amu are due

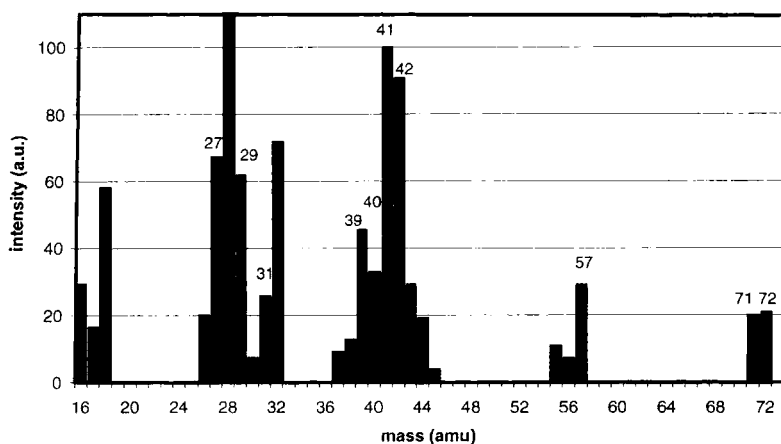


FIGURE 1 Experimental mass spectrum of 1,2-epoxybutane.

to the presence of various species, such as CO and H₂O, coming from the residual atmosphere of every vacuum system and N₂, O₂, CO₂ and H₂O from some amounts of air injected with 1,2-epoxybutane. The remaining peaks at 27, 29, 31, 39, 40, 41, 42, 57, 71 and 72 amu are in agreement with the reference spectrum of 1,2-epoxybutane.

Samples were first outgassed at 1073 K (1023 K for Fe) until the pressure in the reactor was reduced to 10⁻⁶ Torr (needed time about 20–30 min). Epoxybutane was then introduced into the reactor at a pressure of 10 Torr, the sample temperature being maintained at 353 K. This adsorption step was carried out for 10 min. Then, the reactor was evacuated, at the same temperature, through the vacuum line until the residual pressure returned to 10⁻⁶ Torr. Finally, a TPD run was carried out from 353 K up to 1073 K (1023 K for Fe) at a heating rate around 10 K s⁻¹. A consequence of inductive heating was that the walls of the reactor were only heated by radiation emitted by the sample at high temperatures (above 800 K). Therefore, a desorption from the walls of the reactor was observed and was responsible for a regularly-increasing signal of the TPD spectrum, in the range from 850 to 1100 K. When necessary, in order to recover the baseline at high temperatures, spectra were corrected for this background, taking as reference a sample which did not exhibit a desorption peak at high temperatures (pure chromium, for example).

Mechanical Test

Adhesion measurements were performed by a three-point flexure test using the single interface substrate-adhesive specimen described previously [17]. Treated substrates ($50 \times 10 \times 1$ mm) were glued with a two-component epoxy resin (AY103 with amine-containing hardener HY991 from Ciba-Geigy). The adhesive mixing and the bonding were performed at 20°C , 35% r.h. The samples were cured for 2 h at 80°C and allowed to cool for 1 h before being removed from the mould. Then, they were stored for 24 h in a desiccator and exposed to a humid environment (70°C , 95% r.h.) for 72 h before testing. According to the sample size and geometry used, such an aging is long enough to reveal the performance variations between differently treated substrates [24]. The bonded specimens were subjected to a continuous deflection progressing at 0.5 mm min^{-1} . The parameter taken as representative for the bonded joint strength is the ultimate displacement (d_{max}) before sample failure.

RESULTS AND DISCUSSION

Surface Analysis of SS

The main components of bulk 304L SS are iron (70 w. %), chromium (18 w. %), and nickel (10 w. %). As these elements are likely to participate in the formation of the oxide layer, it is of major importance to analyze the top-surface of the treated SS samples. For this purpose, ion scattering spectroscopy (ISS) can provide analytical information on the outermost atomic layer and has been shown as a very powerful tool to study iron-based alloys, as long as the scattered ion is Ne^+ instead of He^+ [25, 26]. The spectra presented in Figure 2 are relative to pure chromium, iron, and nickel, probed with 2 keV Ne^+ ions. The energy separation between each peak is sufficient to allow a semi-quantitative analysis of a SS surface. The peaks are non-symmetrical in shape, mainly due to the isotopic distribution of Ne on the one hand and of metallic atoms on the other hand.

Typical Ne^+ -ISS spectra of SS samples submitted to chemical etching (a), long duration (10 min) oxygen-plasma treatment (b), and anodizing (c), are shown in Figure 3. It is noteworthy that nickel

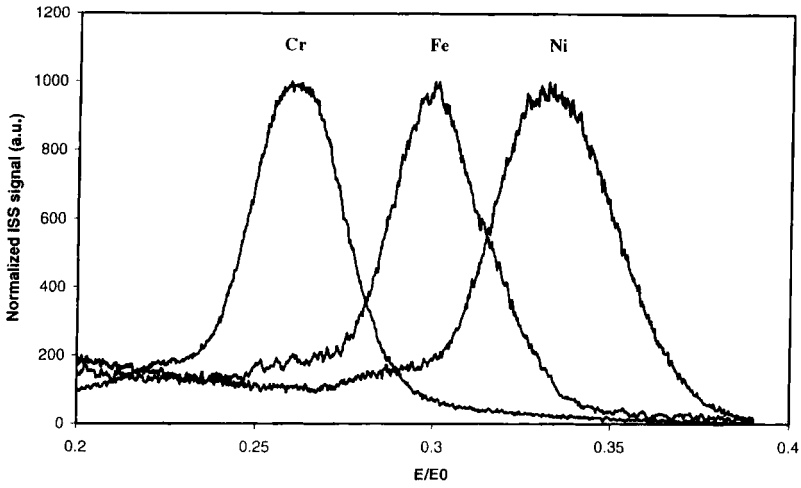


FIGURE 2 ISS spectra of chromium, iron and nickel (2 keV Ne^+ ions).

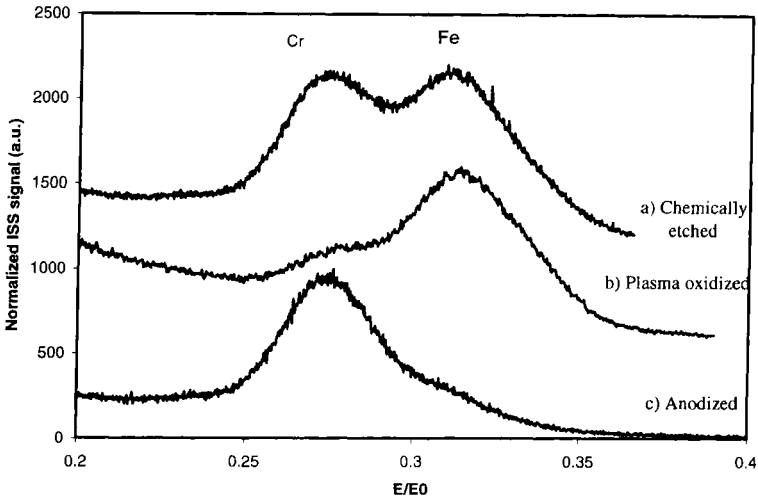


FIGURE 3 ISS spectra (2 keV Ne^+ ions) of SS samples submitted to chemical etching (a), long-duration oxygen plasma treatment (b), and anodizing (c).

cannot be detected at the surface of the SS samples. This confirmed results from a systematic study of SS pre-bonding treatments [24]. Thus, we will consider only iron and chromium for the remainder of

this work. The spectra presented in Figure 3 also show that the Cr/Fe ratio can be varied within a very wide range. Typical samples are a SS submitted to a long duration oxygen-plasma, which is quite fully chromium-depleted, and an anodized SS where only chromium can be detected at the outermost surface. XPS quantitative analysis results indicated a Cr/Fe ratio ranging from about 0.3 in the case of the sample exposed to the long duration oxygen plasma to about 3.5 in the case of the $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ anodized specimen.

Ammonia TPD

First, ammonia adsorption was performed on pure chromium and iron, according to the procedure described previously for 1,2-epoxybutane. The peak at $m/e = 17$ amu was selected to obtain the typical TPD profiles plotted in Figure 4. For temperatures lower than 370 K, no ammonia desorption is observed. This indicates that ammonia, loosely held to the sample surface, was eliminated during the evacuation at 350 K. For chromium (trace *a*), a main broad peak is detected. Its maximum is located at about 500 K and it stretches up to 780 K. The spectrum of iron is quite different since it exhibits three peaks at about 490, 620 and 950 K. In order to discuss the following

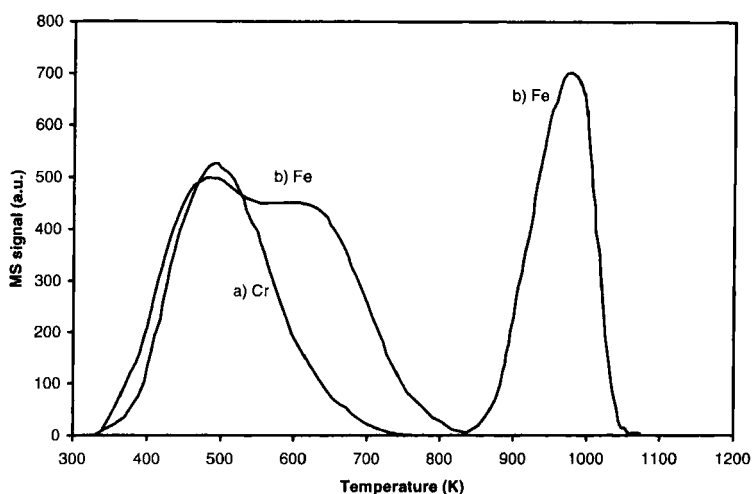


FIGURE 4 Ammonia TPD spectra from pure chromium (a) and iron (b).

results, it is convenient to classify arbitrarily the desorption peaks into three types, I, II and III, corresponding to $T_m < 600$ K, 600 K $< T_m < 900$ K and $T_m > 900$ K, respectively.

SS samples were subjected to various treatments: oxygen plasma (300 s), acid etching, solvent cleaning, nitric acid anodizing (300 and 3600 s) and $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ anodizing. Corresponding Cr/Fe ratios determined by XPS were: 0.03, 0.5, 0.52, 1.35, 2.02, 3.48. The amount of ammonia desorbed is plotted in Figure 5 for each sample, according to the three types defined previously. The total amount of desorbed ammonia increases when the Cr/Fe ratio increases. The only exception is the sample which was subjected to solvent cleaning. This can be explained by the fact that a mere solvent cleaning is not efficient enough to remove hydrocarbon contamination, as shown by the C/(Fe + Cr) ratios determined by XPS and reported in Table II. The ratio is about 18 for the solvent-cleaned sample while it ranges from 2 to 4.7 for the other treatments. This contamination by carbonaceous species can justify the lack of reactivity of this sample toward ammonia molecules. When carbonaceous contamination is maintained under a certain threshold amount, a correlation is clearly observed between the Cr/(Fe + Cr) ratio and the ability of SS surface to adsorb probe

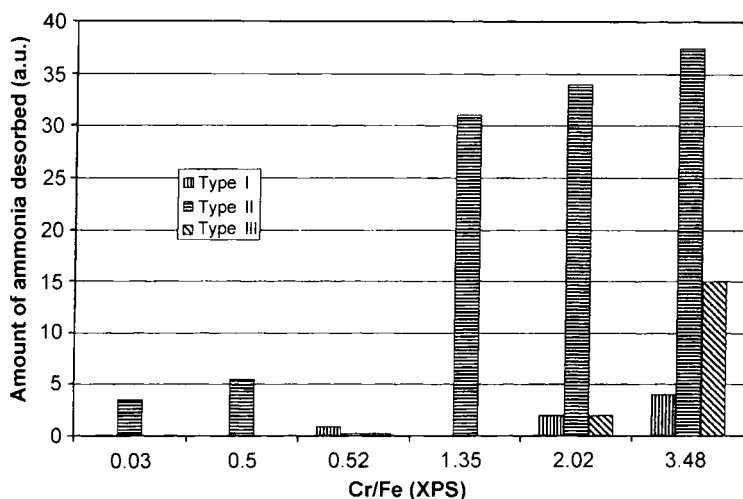


FIGURE 5 Results of ammonia TPD from SS samples with various surface Cr/Fe ratios.

TABLE II C/(Fe + Cr) ratios, determined by XPS, for SS samples subjected to various surface treatments

<i>Treatment</i>	<i>C/(Fe + Cr)</i>
Plasma oxidizing, 300 s	2.9
Chemical etching	2.7
Solvent cleaning	17.5
HNO ₃ anodizing, 300 s	4.7
HNO ₃ anodizing, 3600 s	2.8
H ₂ SO ₄ –K ₂ Cr ₂ O ₇ anodizing	2.0

or model molecules. Previous studies also showed that such a level of carbonaceous contamination was not detrimental to the strength of the bonded joint [27, 28], probably because some active groups of the adhesives are able to displace these organic contaminants [29]. Another interesting fact is that anodized samples with higher Cr/Fe ratios (2.02 and 3.48) exhibit sites of type III, responsible for strong interactions with the basic probe molecule. Such sites were not detected on pure chromium substrates and may be attributed to a particular structure of the thick anodic oxide layers [15].

For temperatures reached at the end of the TPD experiments (over 800 K), ammonia decomposition or dehydrogenation can occur on some materials [30, 31] and could lead to the formation of nitrides. Among the components of SS, iron could favour such a reaction [32] but the presence of metallic sites non-poisoned by O₂ is necessary [33] and such sites are not available under our experimental conditions. Chromium oxide can also favour dehydrogenation. As we were not able to analyse H₂ accurately during the TPD run, we cannot reject the possibility of such a side-effect, which is not likely to modify the main conclusions of this study.

Epoxybutane TPD

Figure 6 shows the TDP spectra obtained with Cr, Fe and SS, the mass spectrometer being set to mass $m/e = 72$, the parent mass peak of 1,2-epoxybutane. The profile for Cr exhibits a wide TPD peak at 620 K with a poorly-marked shoulder around 500 K. The profile corresponding to Fe also exhibits a peak at 620 K, with a tail stretching toward lower temperatures, and another sharp peak at 940 K. It is seen that the TPD spectrum of SS consists of a lower temperature peak at 620 K

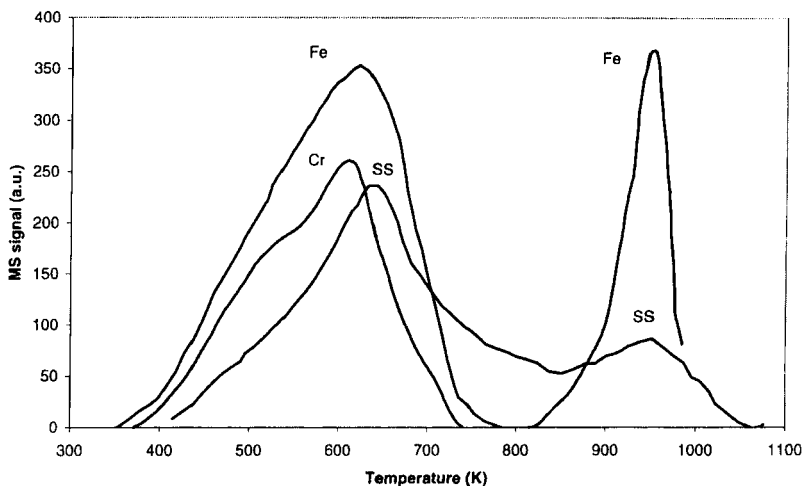


FIGURE 6 Mass 72 TPD profile for Cr, Fe and chemically-etched SS.

after a slow rise up to 550 K, and a higher temperature peak at 950 K. This may be interpreted by a sum of the profiles of Cr and Fe, in agreement with the result of the ISS analysis dealing with etched SS samples (see Fig. 3a).

TPD spectra have also been obtained by recording various mass peaks present in the mass spectrum of 1,2-epoxybutane. It turned out that most of the fragment peaks present in TPD spectra were detected in larger amounts than could be expected from the pure 1,2-epoxybutane fragmentation in the MS source. This means that 1,2-epoxybutane undergoes decomposition reactions at the metal surface before or during TPD. Figure 7 shows, for instance, the spectra obtained by recording the mass peaks $m/e=27$, 41, 57 and 72 during TPD from the Cr sample. In this figure, profiles of masses 27, 41 and 57 have been corrected to account for the fragmentation of 1,2-epoxybutane in the MS source. This was achieved by subtracting the 1,2-epoxybutane contribution based on the profile of the parent peak. The discrepancy between the position of the parent peak $m/e=72$, on the one hand, and peaks resulting from 1,2-epoxybutane surface decomposition on the other hand, confirms that temperature-programmed reactions occur on the metal surface. The maxima of the masses 27, 41 and 57 occur while the concentration of 1,2-epoxybutane decreases in the gas phase.

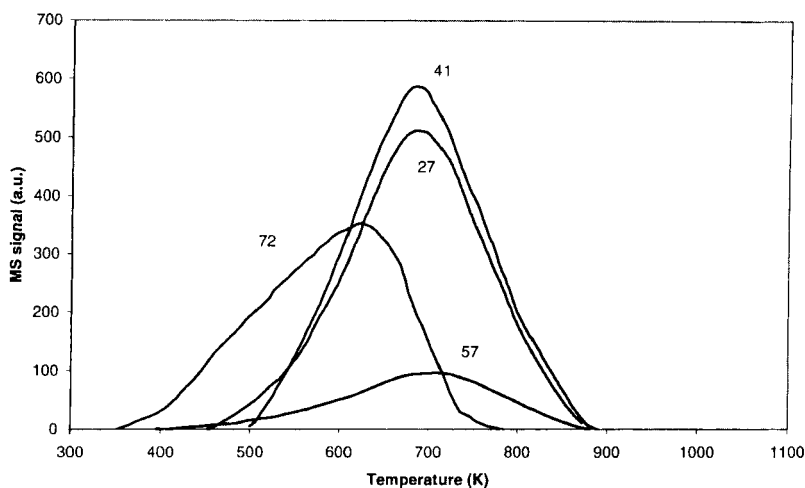


FIGURE 7 TPD profiles (27, 41, 57 and 72 amu) for chromium sample. Profiles of masses 27, 41 and 57 were corrected to account for the fragmentation of 1,2-epoxybutane in the MS source.

This shows that, during its desorption, a part of 1,2-epoxybutane undergoes strong chemisorption (as such or dissociated) on the metal surface, according to a temperature-programmed superficial reaction [34] process. It is also seen that mass peak 57 appears at the beginning of the 1,2-epoxybutane desorption. The same trends have been observed for Fe and SS as for Cr. This strongly suggests that a chemical interaction between 1,2-epoxybutane and the Cr, Fe and SS surfaces takes place at 353 K during epoxybutane adsorption. It is very likely that the epoxy functional group is involved in this chemisorption. Such a behavior was reported on iron oxide, where molecules containing glycidyl were shown to dissociate through C—O bond scission [10]. We tried to confirm this interpretation by FTIR analyses of adsorbed epoxybutane, but the absorption bands were very weak and difficult to detect on SS, which exhibits poor reflective properties. Such difficulties were also encountered by other authors [35] who investigated the chemisorption of epoxyhexane on polished aluminum and concluded the possibility of epoxy ring opening and the formation of alcoholate species, in agreement with the observations of Miyata *et al.* [36]. Such an opening of the epoxy ring is consistent with our TPD results.

FT-IR Analysis of Adsorbed 2(methylamino)ethanol

RAIRS is known to provide analytical information at the sub-monolayer level [37], especially with organic molecules adsorbed on flat metallic surfaces [38, 39]. We used this technique to analyze 2(methylamino)ethanol adsorbed on pure chromium, iron, and on treated SS samples, following the procedure described in the experimental section. Concerning the iron substrate, no adsorption of 2(methylamino)ethanol was detected. A very different behavior was exhibited by pure chromium substrates, where infrared absorption bands characteristic of the adsorbed molecule were detected. This molecule strongly interacts with the surface, as indicated by the bands strongly shifted compared to those of the transmission spectrum of 2(methylamino)ethanol. According to these preliminary observations, we submitted to the same procedure SS samples treated in order to obtain Cr/Fe ratios ranging from 0.5 to 2.02. The corresponding spectra are plotted in Figure 8, in the spectral range from 960 to 1800 cm^{-1} . The samples with the thickest oxide films, obtained by anodizing in $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ medium, were not considered because their reflectivity in the mid-infrared was not sufficient to achieve a good analytical sensitivity. A detailed study of the RAIRS spectra reported here is beyond the scope of this study. One main band at about 1590 cm^{-1} can be detected for $\text{Cr/Fe} \geq 0.84$. The intensity of this band increases when the Cr/Fe ratio increases. This band is attributed to a $\delta(\text{R-N-H})$ vibration and its intensity suggests a dissociative adsorption of 2(methylamino)ethanol, since such a band is usually very weak for secondary amines [40]. These results clearly emphasize that surface chromium enrichment increases the affinity of treated SS surfaces for a molecule which mimics an epoxy adhesive.

Correlation with Adhesion Measurements

Stainless steel samples were submitted to the selected surface treatments, glued with an epoxy resin, conditioned and tested according to the procedure mentioned previously. For the better treatments, the strength of the bonded joints is quite high and, consequently, failure occurs in the non-linear part of the force-deflection curve. Therefore, we considered the ultimate displacement before failure

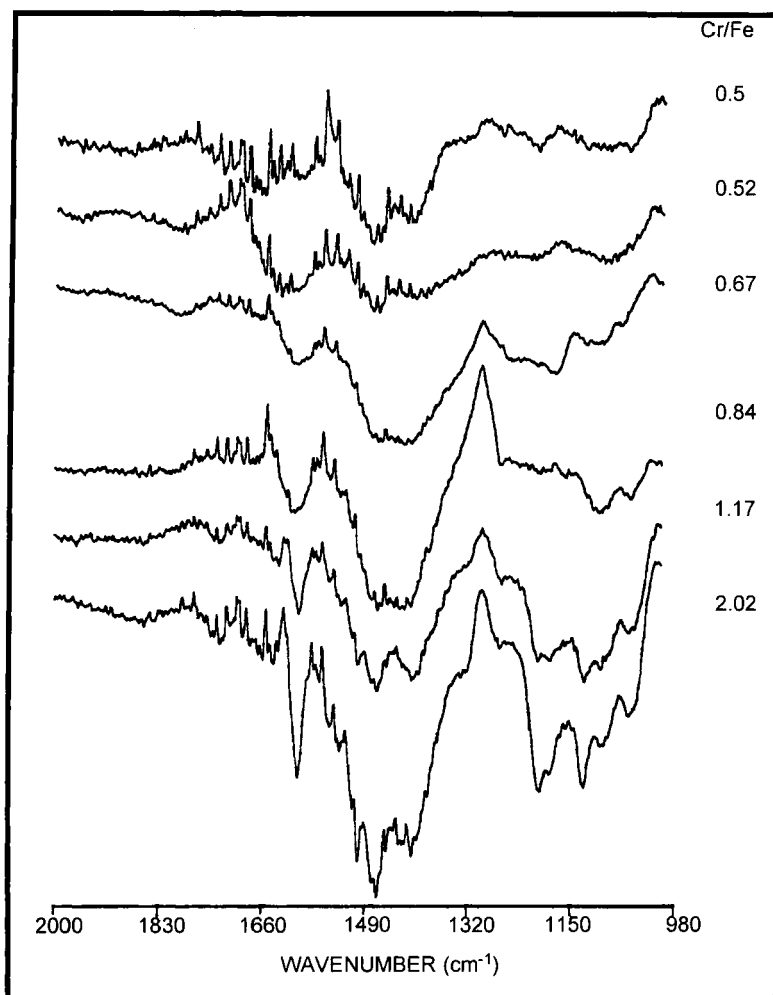


FIGURE 8 FT-IR spectra of 2(methylamino)ethanol adsorbed on SS samples with various surface Cr/Fe ratios.

(d_{\max}) as the parameter representative of the bond strength [17]. The values of d_{\max} versus the Cr/Fe ratio (determined by XPS) are plotted in Figure 9. The amounts of ammonia detected by TPD and of 2(methylamino)ethanol determined by FT-IR are also reported. For $\text{Cr/Fe} \geq 1.2$ the strength of the bonded joint drastically improves and keeps increasing when Cr/Fe increases. It is also noteworthy that the

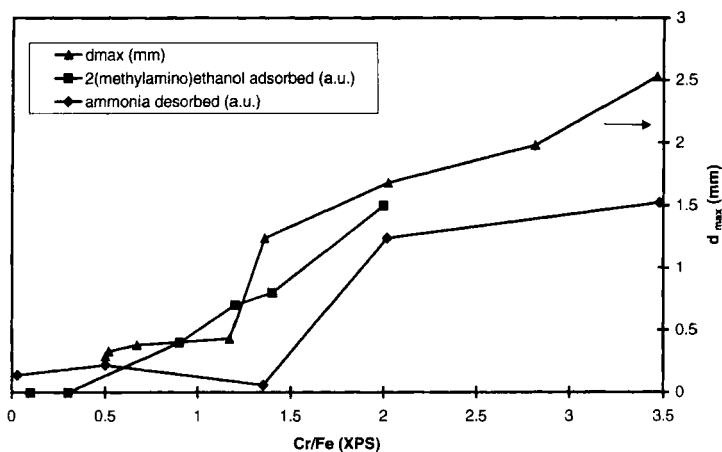


FIGURE 9 The correlation between the bonded joint ultimate deflection (d_{max}), the total amount of ammonia desorbed by TPD, and the amount of adsorbed 2(methylamino)ethanol detected by FT-IR, and the XPS Cr/Fe ratio.

fracture locus (determined by SEM and FT-IR micro-spectroscopy) changes from interfacial to cohesive within the adhesive when Cr/Fe increases. Such a behavior points out the good resistance of the epoxy-SS interfacial zone when appropriate surface treatments are used. These observations have to be compared with Haak and Smith's results [15]. These authors investigated an AM355 steel (15.5% Cr, 4.3% Ni, 2.8% Mo) bonded with a Hysol EA 9628H adhesive (a thin film adhesive with an amine-curing system manufactured by Dexter Co). The durability of the bonded joint was assessed by a wedge test according to the ASTM-D3762-79 procedure at 50°C and 99–100% r.h. Steel samples were subjected to a wide range of chemical and electrochemical treatments and analyzed by AES. The conclusion of the authors was that the bonds stabilize to humidity for Cr/Fe > 1.5. Such a ratio can be reached principally by anodizing in a hot $H_2SO_4 - K_2Cr_2O_7$ or HNO_3 medium. Our results are in full agreement with these conclusions. Moreover, the data gathered in Figure 9 emphasize the existence of a Cr/Fe threshold, at about 1.2. Above this threshold, the surface becomes acidic and is able to engage sufficiently strong bonds with some basic groups of epoxy resins (and of model molecules). This leads to the formation of a strong interfacial zone and a resistant bonded system.

CONCLUSION

Many treatments can be used to modify the surface composition of stainless steels. We selected some chemical, physical and electrochemical treatments known to change the adhesion properties of SS toward epoxy resins. Analysis by ISS and XPS of the so-treated samples indicated that nickel did not participate in the formation of the outermost surface layer of these substrates. Then, we investigated, by TPD and FT-IR, the influence of chromium enrichment of SS surfaces on their reactivity toward molecules (ammonia, 1,2-epoxybutane, and 2(methylamino)ethanol) used to model epoxy resins.

As expected, modified SS surfaces show a mixed behavior between pure chromium and pure iron. When SS surfaces are chromium-enriched, we demonstrated an increase of the density and strength of surface acid sites and an augmentation of the amount of β -amino alcohol adsorbed. Only ammonia TPD spectra of anodized SS samples exhibit peaks at high temperatures (> 900 K), revealing very strong acid sites. Evidence was given for the dissociative adsorption of epoxy compounds. With respect to 1,2-epoxybutane adsorption, SS surfaces follow a behavior reflecting the participation of its iron and chromium constituents. A threshold value $\text{Cr/Fe} = 1.2$ is necessary to obtain an acidic SS surface which can engage sufficiently strong bonds with some basic groups of epoxy resin. As a result, strong and durable epoxy resin-SS bonded joints are promoted.

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