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Molecular Characterization of Multiple Bonding Interactions at the Steel Oxide−Aminopropyl triethoxysilane Interface by ToF-SIMS

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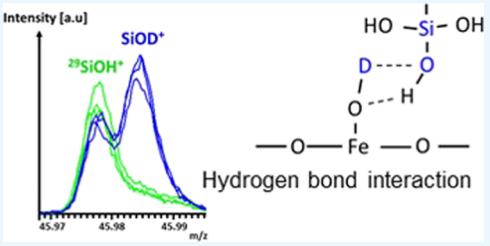
ABSTRACT: Organofunctional silanes are applied as coupling agents between organic coatings and low carbon steel substrates to promote adhesion. Although the metal oxide−silane interface plays an important role in the performance of the entire overlying coating system, it remains challenging to obtain a clear understanding of the interfacial molecular bonding mechanism and its influence on adhesion. In this work, time-of-flight secondary ion mass spectrometry is used to study interfacial interactions between aminopropyl triethoxysilane (APS) and low carbon steel. APS is shown to bond to the steel substrate through silanol steel and amine−steel interactions, and coatings are cured at varying temperatures to evaluate the influence of curing on these different types of bonding interactions. Unambiguous evidence for hydrogen bond interactions between APS silanol groups and steel surface hydroxyl groups is provided for the first time in this work through deuteration of the steel substrate and allows to tackle long-lasting doubts about the most wide-spread bonding theory that has been postulated for silane adsorption on metals.



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1. INTRODUCTION

Organic coatings are generally applied to metal substrates to add corrosion protection and other application-oriented surface properties in a wide range of industries such as construction, aerospace, automotive, packaging, and biomedical healthcare. An important challenge in the industrial coating process is to obtain strong adhesion between the organic primer coating and the metal substrate. Application of the primer coating is mostly preceded by metal surface treatments to enhance adhesion and corrosion protection. Classic pretreatments on (galvanized) steel substrates involved chromate conversion coating and zinc phosphating, but the corrosion protection scheme of steel substrates has undergone a large transition in the last twenty−thirty years. Restrictions on the use of aforementioned environmentally unfriendly systems have been a major driver in this transition, leading to a vast amount of research toward alternative treatments. One of those alternative treatments was found in the application of organofunctional silanes as adhesion promotors.

Organosilanes are referred to as coupling agents because of their ability to attach strongly to metal oxide surfaces as well as to organic coatings. A lot of importance is given to the organic−inorganic interface, given that the hybrid interface is crucial to the performance of the entire coating system. Many studies have been directed toward characterization of interfacial bonding at the metal oxide−silane interface by X-ray photoelectron spectroscopy (XPS)[1−3] and time-of-flight secondary ion spectrometry (ToF-SIMS).[2−7] ToF-SIMS was shown to be most successful to extract information of interfacial chemistry. Gettings and Kinloch studied the organosilane−steel interface and reported an ionic fragment with a nominal mass of 100 u, which could be assigned to $SiOFe^+$.[4] Bexell and Olsson reported a fragment at nominal mass 109 u, characteristic for a silane−zinc interface, which could be assigned to $SiOZn^+$.[5] Several studies involving silane adsorption on aluminum reported a similar fragment at nominal mass 71 u, which could be assigned to $SiOAl^+$.[2,3,5−7] All these $SiOM^+$ fragments, where M stands for metal, were seen as direct evidence for interactions between silanes and metal oxides through formation of covalent metal siloxane bonds. These observations support the bonding mechanism of silanes proposed by Plueddemann,[8] which has been widely acknowledged in the literature and is illustrated in Figure 1. Most used silane compounds contain alkoxy groups, which in presence of water, hydrolyze into silanol groups (−Si−OH) (Figure 1a). Depending on solution parameters such as the solvent, silane concentration, and pH, condensation reactions can occur between two silanols groups, leading to the formation of oligomeric or polymeric structures through siloxane (−Si−O−Si−) bonds (Figure 1b). When the silane solution comes into contact with the metal substrate, silanol groups interact with surface hydroxyl groups through formation of hydrogen bonds (Figure 1c) or by formation of a covalent metal oxane bond (−M−O−Si−). It is suggested that an equilibrium exists between these two bonding configurations after the substrate is removed from the silane solution.

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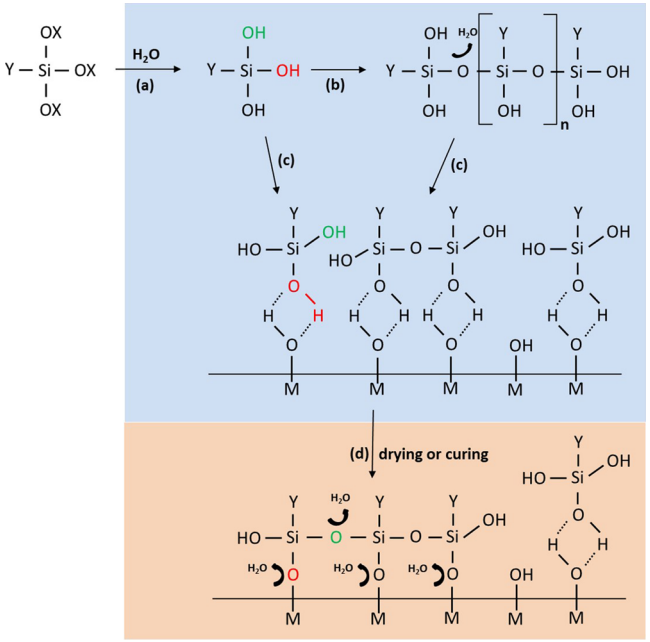

Figure 1. Interfacial bonding mechanism of silanes to a metal surface as it has been often described in the literature, based on the mechanism proposed by Plueddemann.[8] X represents hydrolysable alkoxy groups, Y represents an organofunctional group, and M represents a metal.

Upon drying at room temperature and even more by applying additional heat in a curing step, covalent metal siloxane bonds are formed through a condensation reaction[8] (Figure 1d). Covalent interactions are stronger than hydrogen bond interactions and therefore more desirable with respect to adhesion.[9]

Although the bonding mechanism illustrated in Figure 1 has been often cited in the literature, reactions (c,d) in the mechanism, which involve the actual interactions between the silanes and the substrate, are still under debate. On the one hand, it is questioned whether $SiOM^+$ fragments obtained from ToF-SIMS measurements can be considered as sufficient evidence for covalent bonding.[3,10] On the other hand, direct evidence for hydrogen bond interactions at the metal oxide−silane interface has never been provided. In this work, ToF-SIMS will be applied to study the bonding mechanism of aminopropyl triethoxysilane (APS) on steel. State-of-the-art ToF-SIMS instrumentation, with a mass resolution of 8000 at 29 u (Si^+), allows for a detailed analysis of the interface. Although the surface hydroxyl groups of the steel substrate are very likely to play an important role in the bonding mechanism of silanes,[8] their specific role has always been difficult to probe. Therefore, to highlight the interactions in which they are involved, surface hydroxyl groups will be replaced by surface deuteroxide groups. APS contains three ethoxy groups on one side and an amine functionality on the other side (Figure 2). Through its amine group, APS is able to provide good adhesion to epoxies, polyurethanes, and phenolic-based primer coatings,[11] but one should consider that this amine group

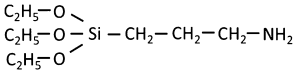

Figure 2. Molecular structure of APS.

might also interact with the steel substrate. Amine-steel interfacial interactions have been characterized before by Wielant et al. with XPS.[12] It was shown that interactions with the substrate occur either through Lewis acid−base interactions, in which there is a donation of nitrogen lone-pair electron density to metal cationic sites, or through Brønsted acid−base interactions, in which amine groups get protonated by surface hydroxyl groups from the substrate (Figure 3). The

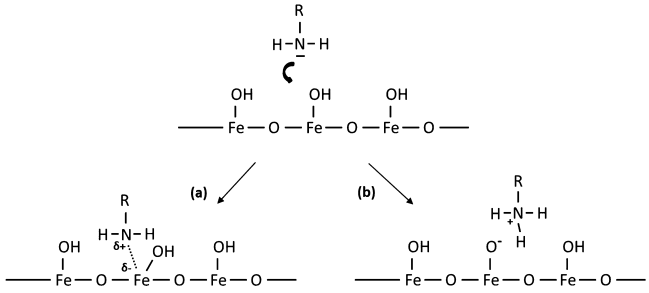

Figure 3. Illustration of the bonding of an amine compound with an iron oxide surface (based on the mechanism proposed by Wielant et al.[12]). (a) Lewis acid base interaction (b) Brønsted acid−base interaction.

main difficulty to probe these interactions with XPS is however that unbound amine groups and Lewis-bonded amine groups give a similar response in XPS binding energies.[12] In this work, it will be evaluated how ToF-SIMS can be used to differentiate between different types of amine steel interactions. Different types of interactions can occur at the steel oxide−silane interface; covalent −M−O−Si− are stronger than amine−steel interactions, and therefore more desired with respect to adhesion.[8] Finally, it has been investigated how variations in curing temperatures influence the interfacial chemistry at the steel oxide−silane interface. The curing temperature is an important parameter in the industrial coating process.

2. EXPERIMENTAL SECTION

2.1. Silane Solution Preparation. A 2 v % silane solution was prepared at room temperature by adding APS (99 atom. %, Sigma-Aldrich) to a solvent mixture of Milli-Q water and methanol (≥ 99.5 atom. %, VWR Chemicals). A 90/10 (v %/v %) water/methanol ratio was chosen, based on a study by Ghosh et al. that evaluated the solvent composition with respect to solution stability and adhesion performance on stainless steel.[13] Wet deposition took place after 1 h of hydrolysis under continuous stirring. The silane solution was always used at its natural alkaline pH (10.4) during the deposition.

2.2. Substrate Preparation. Low carbon cold-rolled steel sheets with a thickness of 500 μm were cut into coupons of 1.5 × 1.5 cm^2 and polished with diamond paste to 0.1 μm roughness. Coupons are cleaned in an ultrasonic bath of ethanol and rinsed with ethanol and milliQ water. Coupons are immersed for 10 min in an 80 wt % NaOH solution at 70 °C. This alkaline pretreatment is based on a study by Wielant et al. on iron oxides[12] and is applied to form surface oxide layers in controllable and reproducible conditions. Deuterated surface oxide layers are generated by immersion of coupons for 10 min in a 40 wt % sodium deuteroxide solution (40 wt % NaOD in D_2O (99.5 atom. % D), Sigma-Aldrich) at 70 °C. After the

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alkaline treatment, coupons are rinsed with Milli-Q water and dried with N_2.

2.3. Silane Deposition. Ultrathin layers of APS were deposited on the steel coupon by immersion into the APS solution for 15 min. After immersion, samples were rinsed with ethanol and dried with N_2. Samples were cured in an oven at 180 °C at varying residence times, resulting in different peak metal temperatures (PMTs). A thermocouple was used to determine the relation between residence time and PMT (Table 1).

Table 1. Relation between Residence Time in an Oven at 180 °C and Peak Metal Temperature

residence time	PMT (°C)
4 s	50
10 s	75
15 s	100
1 min	150
4 min	180

2.4. ToF-SIMS Measurements. ToF-SIMS measurements were performed with a TOF.SIMS 5 system from ION-TOF GmbH (Münster, Germany), using a 30 keV Bi_3^+ primary ion beam operated in the high current bunched mode for high mass resolution (approximately 8000 at 29 u ($^{29}Si^+$)). The lateral resolution achieved in the high current bunched mode is 3 μm. The pulsed ion beam target current was approximately 0.70 pA. Positive ion mass spectra were acquired over a mass range of 1−800 u and calibrated using a list of fragments of known composition. The accuracy of a mass assignment (in ppm) is calculated by taking the absolute difference between the experimental and theoretical mass of a fragment and dividing this number by the experimental mass. Mass spectra were obtained by rastering areas of 100 μm × 100 μm, at 128 × 128 pixels. The analysis time was 60 s, keeping the total ion dose below the static limit of 1×10^{13} ions cm^{-2} $analysis^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Direct Interface Analysis. A pretreated steel substrate and a steel substrate covered with APS were analyzed by ToF-SIMS. Figure 4a shows the spectra in the 0−99 m/z mass range, and Figure 4b shows the 99−210 m/z mass range. More detailed extracts from fragments of interest are presented in Figure 5, where an overlay of three spectra per condition is given to demonstrate the excellent reproducibility of the measurements. Figure 5a shows that Fe^+, with a decreased intensity as compared to uncoated steel, is still strongly present on APS-coated steel. Figure 5b shows APS characteristic fragments Si^+ and CH_2N^+. Given that the depth information from a ToF-SIMS surface analysis falls within the range of 1−5 nm,[14] one can conclude from the simultaneous presence of APS and substrate fragments that the obtained APS film thickness is lower than 5 nm. Consequently, interfacial fragments between the organic layer and the iron oxide are extracted as well. $SiOFe^+$ is a fragment that has been often reported in the literature as a proof for covalent bonding[4] and is also present in the steel-APS spectrum at a nominal mass of 100 u. Besides $SiOFe^+$, also SiO_2HFe^+, SiO_3HFe^+, and $SiO_4HFe_2^+$ are characteristic for the steel-APS spectrum (Figure 4b). A detailed spectrum of $SiOFe^+$ is given in Figure 5c. CH_4NFe^+ is a fragment found at nominal mass 86 u and clearly indicates that amine−steel interactions are taking place at the interface as well (Figure 5d).

3.2. Silanol-Surface Hydroxyl Interactions. Surface hydroxyl groups on metal substrates are known to play a

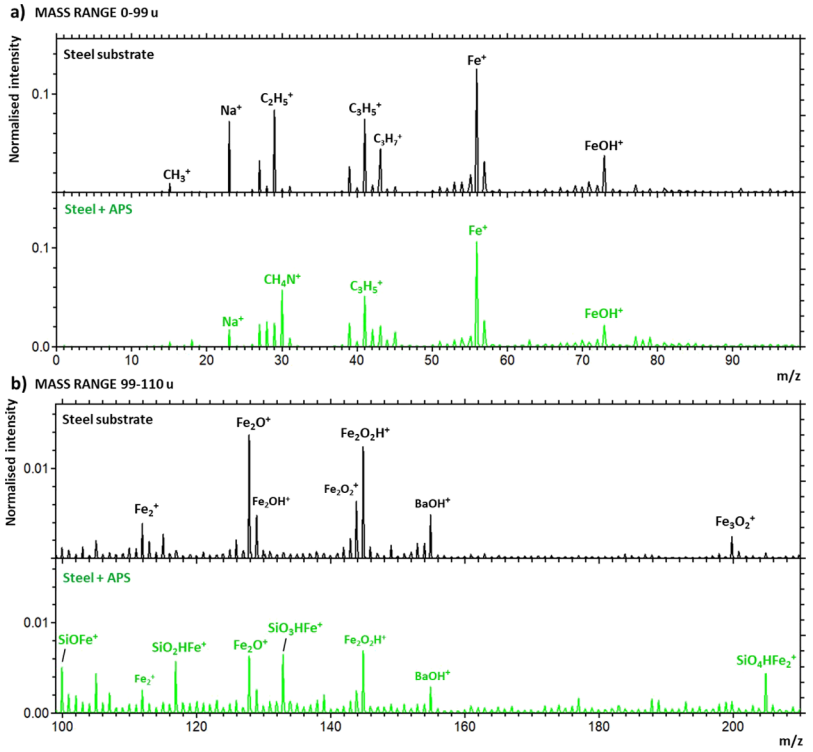

Figure 4. ToF-SIMS overlay of spectra obtained on a pre-treated steel substrate in black and APS coated steel in green (a) in the 0−99 m/z mass range and (b) in the 99−210 m/z mass range.

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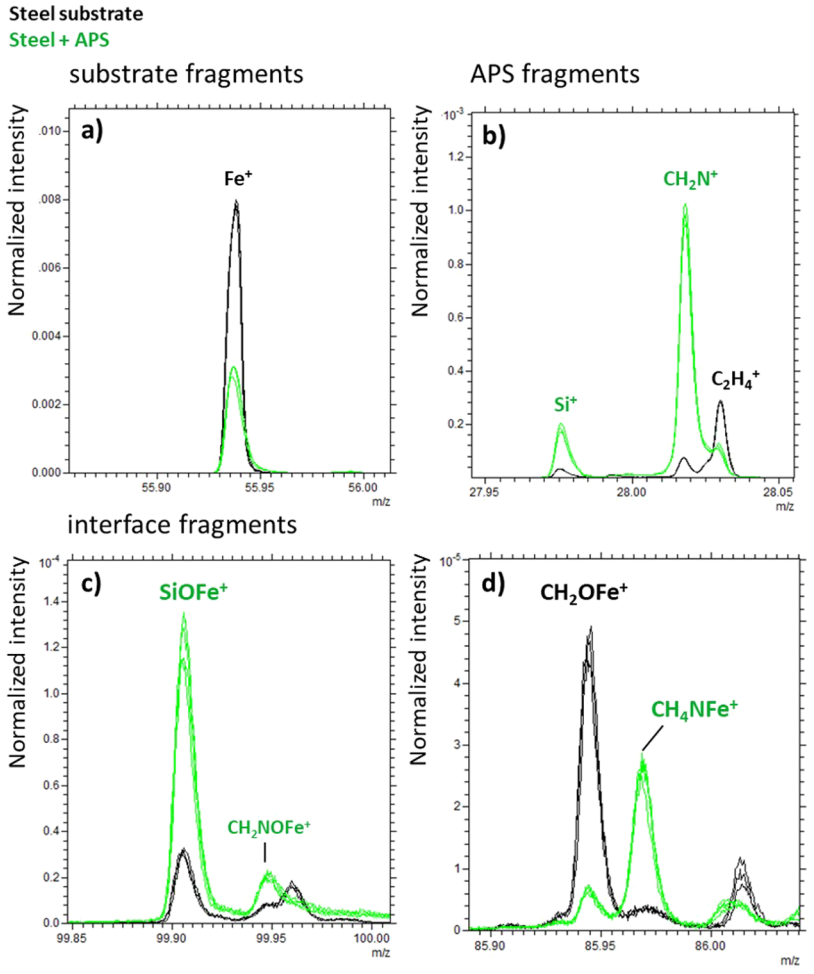

Figure 5. ToF-SIMS overlay of spectra obtained on steel in black and APS-coated steel in green. (a) Fe^+ (b) Si^+ and CH_2N^+ (c) $SiOFe^+$ (d) CH_4NFe^+ three spectra are shown for each condition.

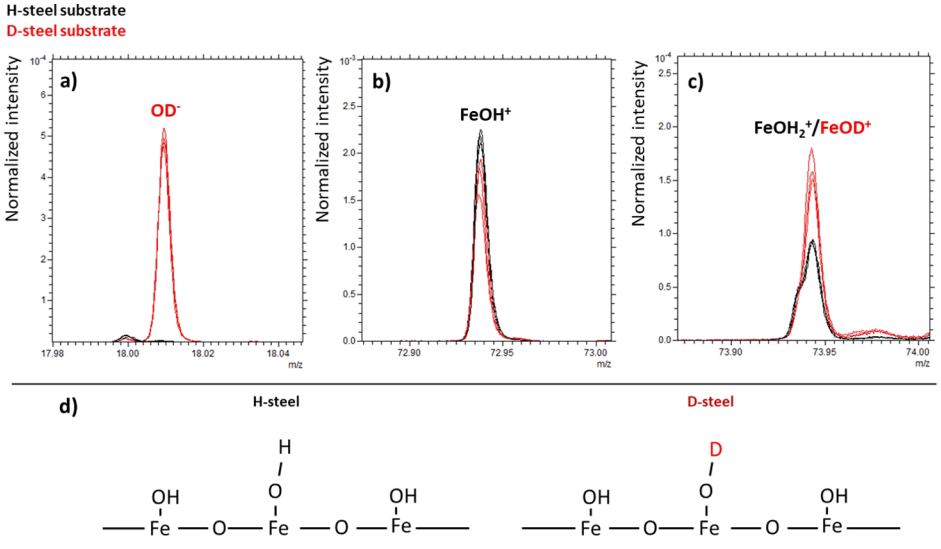

Figure 6. ToF-SIMS overlay of spectra obtained on H-steel in black and D-steel in red. (a) OD^- (b) $FeOH^+$ (c) $FeOH_2^+/FeOD^+$. Three spectra are shown for each condition. (d) Steel surface treated with NaOH (left), steel surface treated with NaOD (right).

major role in the bonding mechanism of organic compounds,[12,15,16] but are not easily probed. In this work, deuterium is applied to investigate the role of surface hydroxyl groups in the adsorption mechanism of APS. Basically, steel substrates were pretreated with NaOD instead of NaOH in order to form surface deuteroxide groups instead of hydroxyl groups. Hereafter, a steel substrate pretreated with NaOH will be referred to as H-steel and a substrate pretreated with NaOD

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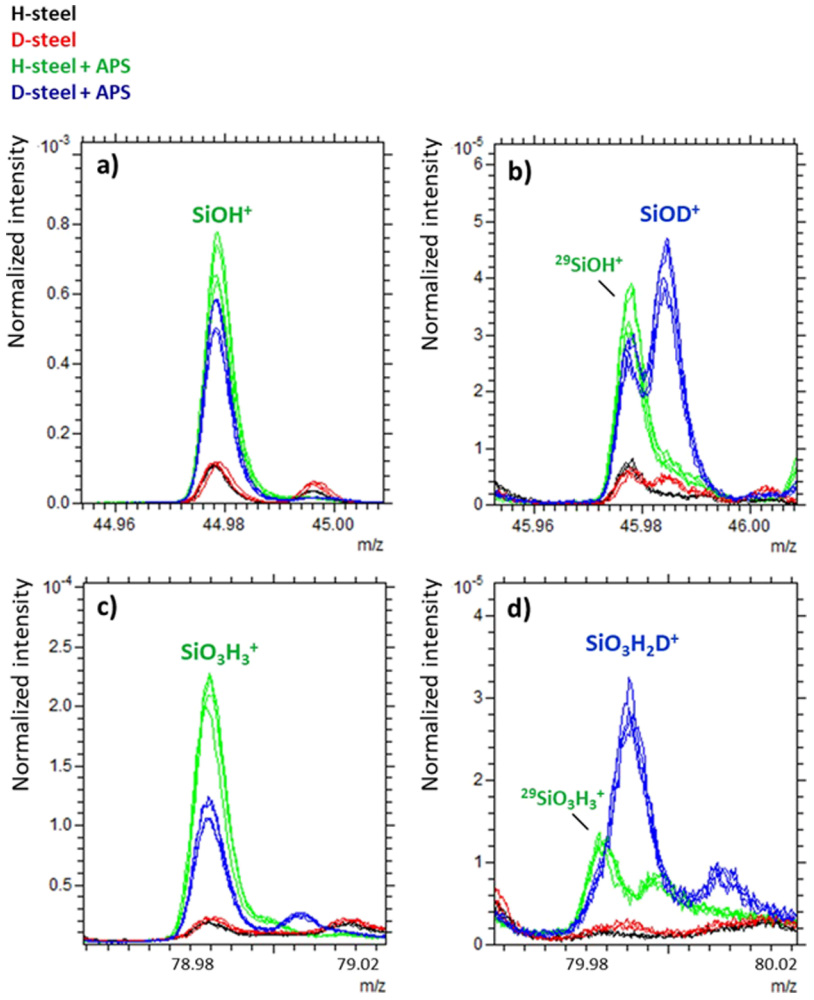

Figure 7. ToF-SIMS overlay of spectra obtained on H-steel in black, D-steel in red, APS-coated H-steel in green, and APS-coated D-steel in blue. (a) $SiOH^+$ (b) $SiOD^+$ (c) $SiO_3H_3^+$ (d) $SiO_3H_2D^+$ Three spectra are shown for each condition.

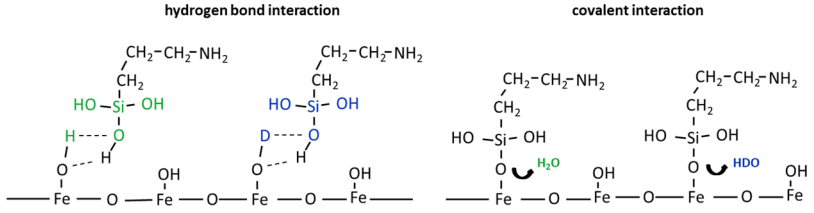

Figure 8. Illustration of hydrogen bond interactions (left) and covalent interactions (right) between APS and steel.

will be referred to as D-steel. Figure 6 compares H-steel with D-steel. In the negative polarity ToF-SIMS spectra, an OD^- peak is only present for the spectrum obtained on D-steel (Figure 6a). Given that all coupons were rinsed with Milli-Q water after the alkaline treatment to remove any NaOH or NaOD precipitates, this is a first indication that deuteroxide anions have reacted with the surface. In positive polarity, the $FeOH^+$ peak at a nominal mass of 73 u (Figure 6b) is found with comparable intensities on both samples. However, a significant increase in intensity on D-steel is observed for a peak originally assigned to $FeOH_2^+$ (Figure 6c). This intensity increase can be attributed to $FeOD^+$ and shows that a certain amount of surface deuteroxide groups were created on D-steel, among surface hydroxyl groups which also remain present, as illustrated in Figure 6d. Surface hydroxyl groups on D-steel may have been there already before the alkaline treatment, or they may have been formed during rinsing with Milli-Q water after the alkaline treatment.

After an evaluation of the two pretreatments, both types of substrates were covered with APS and analyzed with ToF-SIMS. Figure 7 gives an overlay of mass spectra obtained on H-steel, D-steel, APS-coated H-steel, and APS-coated D-steel. While $SiOH^+$ (at 45 u) shows comparable intensities on APS-coated H-steel and D-steel (Figure 7a), an additional peak shows up at a nominal mass of 46 u on APS-coated D-steel (Figure 7b). The latter peak can be identified as $SiOD^+$ and provides direct evidence that an interaction is taking place between silanol groups of APS and the surface hydroxyl groups on steel. A similar isotope pair is found at nominal masses 79 and 80 u, where two peaks are attributed to $SiO_3H_3^+$ and $SiO_3H_2D^+$, respectively (Figure 7c,d). $SiOD^+$ and $SiO_3H_2D^+$ are two fragments indicative for hydrogen bond interactions

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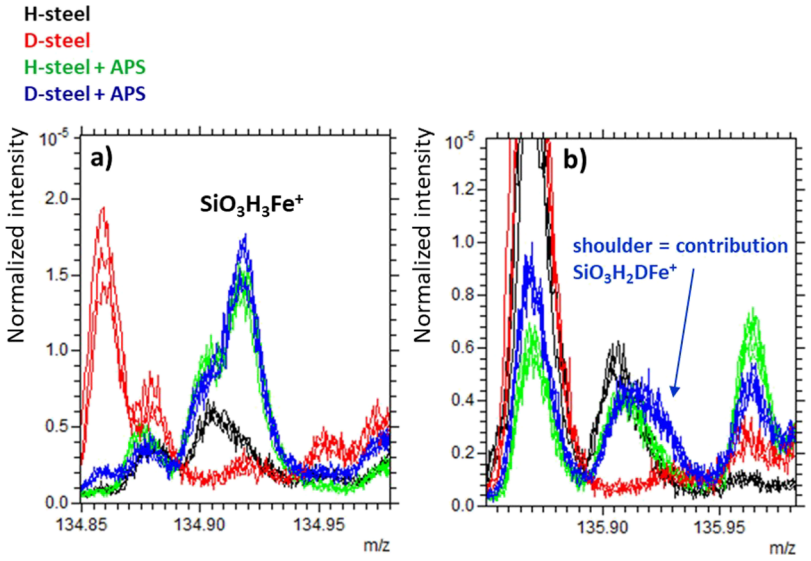

Figure 9. ToF-SIMS overlay of spectra obtained on H-steel in black, D-steel in red, APS-coated H-steel in green, and APS coated D-steel in blue. (a) $SiO_3H_3Fe^+$ (b) $SiO_3H_2DFe^+$. Three spectra are shown for each condition.

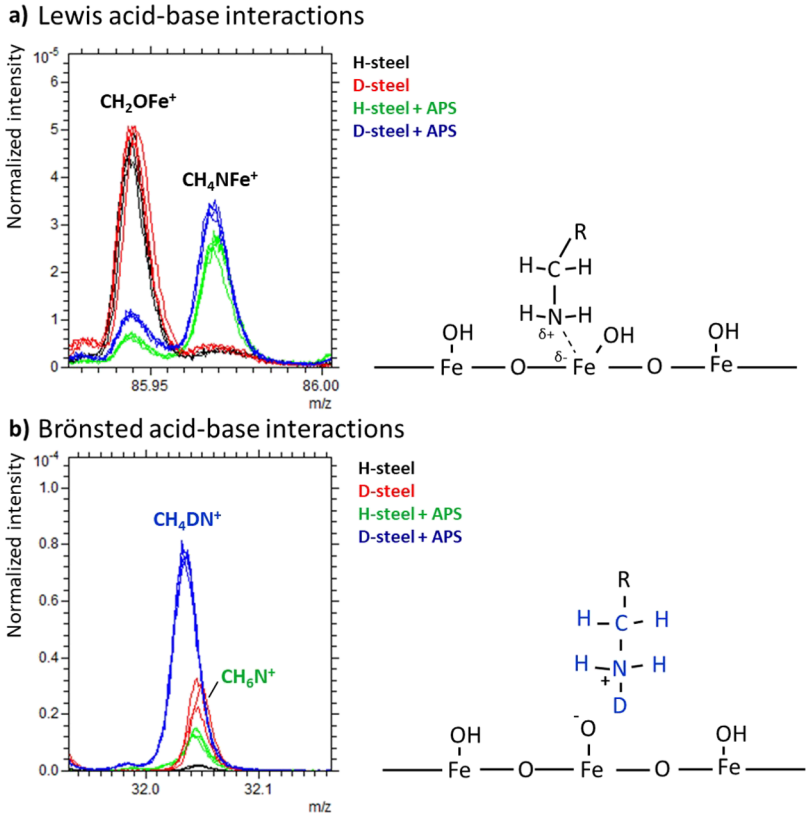

Figure 10. ToF-SIMS overlay of spectra obtained on H-steel in black, D-steel in red, APS-coated H-steel in green, and APS-coated D-steel in blue. (a) CH_4NFe^+ is a fragment characteristic for Lewis type acid−base interactions (b) CH_4DN^+, significantly present on APS-coated D-steel, indicates protonation of the amine group by surface hydroxyl groups of steel. Three spectra are shown for each condition.

between silanol groups and surface hydroxyl groups. This becomes clear from the illustrations in Figure 8, where hydrogen bond interactions are shown on the left-hand side and covalent bond interactions on the right-hand side. One can conclude from this experiment that the $SiOH^+$ and $SiO_3H_3^+$ peaks obtained on APS-coated H-steel contain a certain contribution from hydrogen bond interactions with the substrate. $SiO_3H_3^+$ is more exclusively linked to hydrogen bond interactions as compared to $SiOH^+$ because $SiOH^+$ can originate from hydrogen bond interactions as well as from covalent bond interactions (Figure 8). This explains why the intensity drop upon deuteration of the substrate is more pronounced for $SiO_3H_3^+$ and less for $SiOH^+$ (Figure 7a,c).

At a nominal mass of 135 u, a peak present on APS-coated steel is attributed to $SiO_3H_3Fe^+$ (Figure 9a). Given that the ratio of oxygen to hydrogen in this fragment is 1:1, it is unlikely

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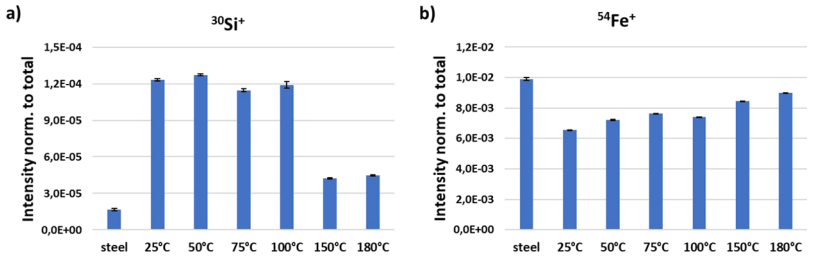

Figure 11. ToF-SIMS intensities of fragments of interest obtained on APS-coated H-steel in function of PMT during a curing step. (a) Si^+ and (b) $^{54}Fe^+$ intensities normalized to total.

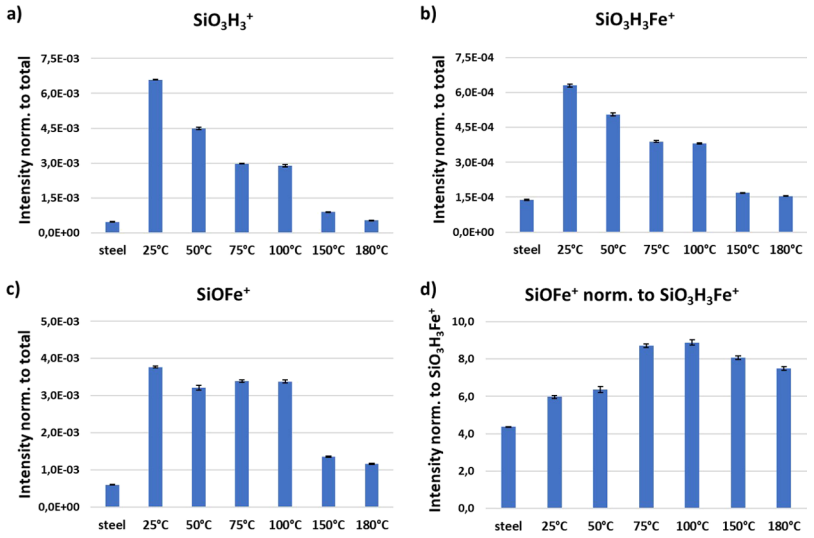

Figure 12. ToF-SIMS intensities of fragments of interest obtained on APS-coated H-steel in function of PMT during a curing step. (a) $SiO_3H_3^+$ and (b) $FeSiO_3H_3^+$ intensities normalized to total. (c) $SiOFe^+$ intensities normalized to total and (d) $SiOFe^+$ intensities normalized to $SiO_3H_3Fe^+$.

that this fragment is attributed to covalent bonding. The shoulder on a peak observed at 136 u for APS coated D-steel suggests that surface hydroxyl groups are involved in this fragment (Figure 9b). Although at this point it is difficult to assign this fragment to one single structure unambiguously, it is likely that this fragment is largely attributed to hydrogen bond interactions.

3.3. Amine−Steel Interactions. At a nominal mass of 86 u, a peak attributed to CH_4NFe^+ indicates that amine−steel interactions are taking place at the interface (Figure 10a). CH_4NFe^+ intensities on APS coated H-steel are comparable to those obtained on APS-coated D-steel. The absence of oxygen in the fragment tells us that the interaction occurs between the free electron pair of nitrogen and iron. This corresponds to Lewis type acid−base interactions, as described in the literature[12] and illustrated in Figure 10a. On APS-coated D-steel, an additional peak found at a nominal mass of 32 u is attributed to CH_4DN^+ (Figure 10b). This fragment indicates that amine groups of APS are protonated through an acid−base interaction with the steel surface hydroxyl groups. This type of interaction is known as a Brønsted type acid−base interaction and is illustrated in Figure 10b.

3.4. Influence of Curing on Interfacial Bonding. APS coated H-steel samples were cured at varying PMTs to investigate the influence of curing on interface interactions. Different residence times in an oven at 180 °C lead to a variation of PMTs from 25 to 180 °C. Figure 11a shows the intensity variations for $^{30}Si^+$. From 25 to 100 °C, $^{30}Si^+$ intensities are relatively comparable. Between 100 and 150 °C, a sudden decrease in intensity is observed. This significant intensity drop is not only observed for $^{30}Si^+$ but for all APS characteristic fragments. Studies in the literature on the influence of curing temperature on thick (>100 nm) APS and bis-1,2-(triethoxysilyl)ethane (BTSE) coatings reported a thickness decrease and densification of the coatings in the 100−200 °C temperature range,[17,18] attributed to cross-linking of silanol groups which condensate to siloxane (−Si−O−Si−) chains (Figure 1d). Below 100 °C, cross-linking did not occur.

From this information, the significant decrease in intensities for APS characteristic fragments can be explained by a change of the chemical matrix. In ToF-SIMS, secondary ion intensities are influenced by the chemical composition of the surrounding matrix material (SIMS matrix effect). Although ToF-SIMS cannot provide intrinsic quantitative data because of the SIMS matrix effect, it is possible to compare analyses of samples with similar chemistry.[19] APS coatings treated in the temperature range 25−100 °C are not cross-linked and thus can be easily compared. For APS coatings treated at higher temperatures (150−180 °C), one should bear in mind that the chemical matrix has changed because of cross-linking, which seems to result in a significant intensity decrease of APS characteristic fragments. Figure 11b shows the intensity variations for $^{54}Fe^+$, a substrate fragment. $^{54}Fe^+$ intensities are significantly lower on coated samples as compared to the steel substrate. Amongst the coated samples, slightly increased $^{54}Fe^+$ intensities are observed for samples treated at 150−180 °C. This can also be explained by a densification and decrease in thickness of APS layers in this temperature range.

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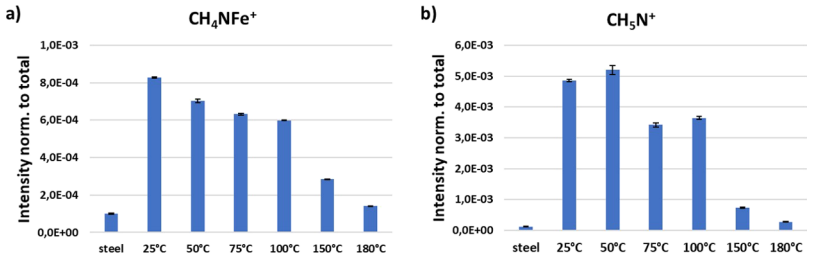

Figure 13. ToF-SIMS intensities of fragments of interest obtained on APS-coated H-steel in function of PMT during a curing step. (a) CH_4NFe^+ (b) CH_5N^+ intensities normalized to total.

When $SiO_3H_3^+$ intensities are plotted against PMT, a clear trend becomes visible (Figure 12a). The highest $SiO_3H_3^+$ intensity is found at 25 °C and gradually decreases when temperature increases to 75 °C. Between 75 and 100 °C, its intensity appears to remain relatively constant. At 150 °C, the $SiO_3H_3^+$ intensity decreases again. Remarkably, $SiO_3H_3Fe^+$ shows the exact same trend as $SiO_3H_3^+$ (Figure 12b), which points out that both fragments are structurally related. Because it was shown in a previous section that $SiO_3H_3^+$ is largely attributed to hydrogen bond interactions at the interface, one can assume that the trend observed for both fragments gives us direct information about hydrogen bonding. Hydrogen bond interactions seem to be most present in the absence of any heat treatment but are strongly diminished by heating to up to 75 °C. The additional intensity drop observed at 150 °C is likely attributed to loss of adsorbed APS species because of volatilization. $SiOFe^+$ intensities are plotted against PMT in Figure 12c but do not show a clear trend. $SiOFe^+$ intensities seem to be largely affected by the amount of Si or coverage of APS, as a large correlation exists with the $^{30}Si^+$ intensities plotted in Figure 11a. However, a significant difference with respect to the $^{30}Si^+$ intensities is that the highest $SiOFe^+$ intensity is observed at 25 °C. This result seems contradictory to the literature, where $SiOFe^+$ is reported as evidence for covalent bonding[4] because Figure 12a,b just showed that the amount of hydrogen bonding is highest at 25 °C. A possible explanation for this observation may be that hydrogen bond interactions and covalent bond interactions are both forming $SiOFe^+$ in their fragmentation patterns. This means that one should not assume that $SiOFe^+$ is a pure evidence for covalent bonding. However, to subtract the contribution from hydrogen bonding, $SiOFe^+$ intensities can be normalized to $SiO_3H_3Fe^+$ intensities (Figure 12d). Relative to $SiO_3H_3Fe^+$, $SiOFe^+$ intensities are highest after heating up to 75−100 °C. As this trend is now solely attributed to covalent bonding, one can conclude that the number of covalent bonds is relatively low at low temperatures (25−50 °C) but increases significantly in the temperature range 75−100 °C. This means that condensation reactions at the hybrid interface, which convert the hydrogen bond interactions to covalent −Si−O−Fe− bonds, occur at lower temperatures than the cross-linking of silanol groups in the bulk of the coating.

CH_4NFe^+ intensities plotted against PMT in Figure 13a show a clear trend. CH_4NFe^+ intensities are highest at 25 °C and gradually decrease with increasing curing temperature. Therefore, one can state that Lewis type acid−base interactions at the interface diminish with increasing curing temperature. Brønsted acid−base interactions between the APS amine groups and steel surface hydroxyl groups are represented by CH_5N^+ (Figure 13b). Brønsted acid−base interactions are most present at 50 °C but seem to diminish significantly at higher curing temperatures.

4. CONCLUSIONS

Although for a very long time it has been postulated that hydrogen bonding occurs at the silane-metal oxide interface, direct evidence for hydrogen bond interactions has been provided in this work for the first time. Deuteration of steel surface hydroxyl groups allowed us to distinguish between interactions attributed to hydrogen bonding and covalent bond interactions. One must be careful with interpretation of $SiOFe^+$, a fragment that has been repeatedly reported in the literature as evidence for covalent bonding, as it was shown that both hydrogen bonding and covalent bonding contribute to $SiOFe^+$ intensities. ToF-SIMS may not be able to quantify these multiple interactions in an absolute way, but can indicate how certain interactions evolve in function of a varying process parameter. This was shown by varying the curing temperature. Hydrogen bond interactions were most present in the absence of curing and gradually diminish upon curing to 75 °C. To a similar extent, the amount of covalent interactions increases with increasing curing temperatures up to 75 °C. These observations confirm the theory that hydrogen bond interactions are converted to covalent bond interactions through a condensation reaction which is promoted by applying heat. Evidence for amine−steel interactions is also found in the form of the Lewis type and Brønsted type acid−base interactions. Both interactions were shown to diminish with increasing curing temperature. The curing of silane coatings is an important industrial step in view of promoting interfacial adhesion and coating barrier properties. Barrier properties are improved by condensation of silanol groups, resulting in a cross-linked −Si−O−Si− siloxane network. Covalent −Si−O−Fe− interfacial bonds are favorable over hydrogen bond interactions and amine−steel interactions in terms of adhesion performance. This work points out that condensation reactions at the hybrid interface, which convert the hydrogen bond interactions to covalent −Si−O−Fe− bonds, occur at lower temperatures (50−75 °C) than the cross-linking of silanol groups in the bulk of the coating, which only occurs at temperatures above 100 °C.

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■ ABBREVIATIONS

APS, aminopropyl triethoxysilane; ToF-SIMS, time-of-flight secondary ion mass spectrometry; XPS, X-ray photoelectron spectroscopy; PMT, peak metal temperature

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