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Understanding Organic Film Behavior on Alloy and Metal Oxides

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Abstract

Native oxide surfaces of stainless steel 316L and Nitinol alloys and their constituent metal oxides namely, nickel, chromium, molybdenum, manganese, iron and titanium were modified with long chain organic acids to better understand organic film formation. The adhesion and stability of films of octadecylphosphonic acid, octadecylhydroxamic acid, octadecylcarboxylic acid and octadecylsulfonic acid on these substrates was examined in this study. The films formed on these surfaces were analyzed by diffuse reflectance infrared Fourier transform spectroscopy, contact angle goniometry, atomic force microscopy and matrix assisted laser desorption ionization mass spectrometry. The effect of the acidity of the organic moiety and substrate composition on the film characteristics and stability is discussed. Interestingly, on the alloy surfaces, the presence of less reactive metal sites does not inhibit film formation.

Introduction

Self assembled monolayers (SAMs) of thiols on gold and silanes on silicon have been model systems for numerous applications including adhesion¹, corrosion inhibition², biomaterials^{3, 4}, biosensors⁵, wettability⁶, click-chemistry⁷ and organic electronics.⁸ The structure and conformation of thin films of thiols on gold are based on the strong interaction between sulfur and gold. These SAMs present functional tail groups in a consistent manner allowing the films to be used in a variety of applications^{9–12}. While forming SAMs on metals and alloys relevant to a particular biomedical or industrial application represents a more straightforward approach to functionalizing these materials, the chemistry of these surfaces has not been as well-studied, in most cases, and is therefore not predictable.

Modification of metal oxide surfaces by organic monolayer formation has been studied since Nuzzo and Allara's seminal work in the 1980's.¹³ Since then, many metal oxides such as aluminium^{13, 14}, copper^{14–16}, nickel^{8, 17}, titanium^{16, 18, 19}, zirconium,^{18, 20} tantalum²¹, silicon,^{22, 23} mica²⁴, silver^{14, 16}, iron^{2, 16, 25}, manganese and chromium²⁶ have been used as substrates to form SAMs. The choice of head group is critical for the stability of SAMs. Long chain aliphatic molecules with head groups such as silanes,^{27, 28} thiols,^{29, 30} carboxylic acid,^{13, 31–35} phosphonic acid,^{36–39} sulfonic acid,^{39, 40} and hydroxamic acid^{16, 41} have been utilized on these metal and metal oxide substrates. Despite a significant number of reports of SAMs on metal oxides, it is difficult to predict which head group or acid will result in a complete monolayer on a specific metal substrate. This has been proven to be even more difficult on alloy oxides, where little work has been done.^{27, 36, 37, 42–44}

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Supporting Information Available: Additional MALDI-TOF, AFM and contact angle data is available in supporting information as noted in the text. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

Stainless steel 316L is a low-carbon austenitic steel which is used as surgical implant material. Like all stainless steels, it contains a minimum of 12% Cr to aid in the formation of protective surface layer which resists corrosion in a wide range of environments, but is also less susceptible to sensitization and more resistant to chloride-assisted corrosion due to its lower carbon content and alloying with Mo and Mn. Whereas SS316L is a conventional alloy, Nitinol is a less-utilized alloy which has gained popularity in the field of biomaterials due to its shape memory property and corrosion resistance.^{45–47} Modifying these substrates has been proven to be challenging perhaps because only some of the surface species in the alloy react with the organic. On other metal oxide surfaces incomplete film coverage has been attributed to many parameters including low hydroxyl content, surface roughness^{48, 49} and surface defects⁴⁹.

In this study, monolayer formation on the alloy oxide surface of SS316L and Nitinol was compared to monolayer formation on the constituent metal oxide surfaces, iron, nickel, titanium, chromium, molybdenum and manganese by long chain aliphatic acids with various head groups (sulfonic acid, phosphonic acid, hydroxamic acid and carboxylic acid). The extent of monolayer formation in these systems was studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS), contact angle goniometry and atomic force microscopy (AFM), in order to elucidate the role of constituent metals and head group in monolayer formation on alloys.

Experimental

Materials

Stainless Steel foils (SS316L, 99.99% pure), molybdenum foils (99.9% pure), iron foils (99.5% pure), nickel foils (>99% pure) and titanium foils (>99% pure) of 0.25mm thickness were obtained from Goodfellow Inc. Chromium pieces of 1mm–6mm size (99.998% pure) and manganese pieces of 3mm–12mm size (99.99% pure) were obtained from Kurt J. Lesker Company. Nitinol foils (NiTi, 51% nickel: 49 % titanium; 0.008” thickness, >99.0 % pure) were purchased from Johnson Matthey, Inc. Tetrahydrofuran (Optima grade), methanol, octadecylcarboxylic acid (ODCA, 98+ %) were obtained from Aldrich Chemical Co. Tetrahydrofuran (THF) was distilled over sodium and stored under nitrogen. Octadecylphosphonic acid (ODPA, 98%) was obtained from Alfa Aesar. Octadecylhydroxamic acid (ODHA) was synthesized in the laboratory as previously reported.¹⁶ Sodium 1-octadecanesulfonate (97%) was obtained from Fluka and acidified using hydrochloric acid to form the corresponding acid. The octadecylsulfonic acid (ODSA) formed was then analyzed by IR, mass spectrometry and NMR. Hydrochloric acid (ACS certified Plus) was purchased from Fisher Scientific and used without further purification.

Equipment

All diffuse reflectance infrared spectroscopy (DRIFT) measurements were performed on a Nexus 470 FTIR equipped with a diffuse reflectance attachment from Thermo Electron Corporation. Contact angle measurements were obtained on a VCA Optima Goniometer. Atomic force microscope (AFM) images were taken on a PicoSPM from Molecular Imaging Corporation (Agilent Technologies). Mass spectra were collected on a high resolution atmospheric pressure time-of-flight mass spectrometer purchased from Agilent Technologies.

Substrate preparation and monolayer formation

Stainless steel 316L (SS316L), Nitinol (NiTi), iron, nickel, titanium and molybdenum substrates were cut into 1 cm × 1 cm coupons and sanded using 220, 320, 400 and 600 grit silicon carbide papers. Manganese and chromium pieces were ingots and therefore not sanded because of their morphology. All substrates were cleaned by ultra-sonication in methanol (15

min) followed by immersion in boiling methanol to remove organic residue and metallic dust. The cleaned substrates were stored in an oven at 100°C.

Films were formed on the native oxide surface of the two alloys and their constituents using solution deposition methods (either dipping or spraying).^{17, 32, 36, 37} The experimental procedure used to form monolayers for each of the metal /alloy- acid combination is tabulated in Table 1. The final procedures were arrived at by varying experimental procedures including increasing the deposition time, organic concentration, deposition temperature, and solution deposition method in an attempt to obtain successful film formation. Numerous unsuccessful procedures were performed and not included in the manuscript. The procedures adopted to form monolayers are as discussed below. All substrates were stored at 100°C prior to deposition.

1. The substrates were sprayed using a 0.35mM solution of the acid at room temperature and allowed to dry at room temperature.
2. The substrates were sprayed using a 0.75mM solution of the acid at room temperature and allowed to dry at room temperature for 20 minutes and then the same spraying procedure was repeated one more time.
3. A 1.5mM solution was used to spray the substrates 3 times at room temperature and dried in the oven at 120°C for 20 minutes between sprays.
4. Substrates were dipped in 1mM solution of the acid at room temperature for 1 minute.
5. Substrates were left in a 1mM solution of the organic acid for 3–5 minutes at room temperature.
6. Substrates were dipped in a warm (50°C) 1mM solution of the acid for 2 hours and then dried in the oven at 100°C overnight.
7. Substrates were placed on a dish which was then placed in an ice bath for 1 hour. The substrates were then dipped in a warm (50°C) 1mM solution of the acid for 2 hours, taken out of solution without solvent meniscus and stored in the oven at 100°C overnight.
8. Substrates were placed on a dish which was then placed in an ice bath for 1 hour. The substrates were then dipped in a warm (50°C) 2 mM solution of the acid for 2 hours, taken out of solution without solvent meniscus and stored in the oven at 100°C overnight.
9. Substrates were placed on a dish and the dish was placed in an ice bath for 1 hour. The substrates were then dipped in a warm (50°C) 2 mM solution of the acid for 2 hours, taken out of solution with solvent meniscus and stored in the oven at 100°C overnight.

The monolayers were checked for ordering of the alkyl chains by IR and contact angle to confirm condensed film formation. Contact angle data and AFM imaging of dipping and spraying procedures showed similar organization of the films on the surface.

Characterization of the monolayers

Infrared Spectroscopy—After the formation of monolayers, DRIFT was used to analyze the ordering and orientation of the molecules in the monolayer formed. Spectra were collected under nitrogen for 1024 scans with a resolution of 1 cm⁻¹ on each sample and ratioed with a background reference spectrum of the same metal or alloy. After verifying the presence of films after the deposition, the samples were rinsed in THF for 15 mins and analyzed by DRIFT

spectroscopy again to confirm the presence of the films. The substrates were then sonicated in THF for 15 mins to test the mechanical stability of the films.

Contact Angle Measurement—Static contact angle of water on the films was measured to determine the wettability of the surface. The average contact angle value and standard deviation of six measurements each on at least three samples (eighteen measurements total) has been reported.

Atomic Force Microscopy—An atomic force microscope (AFM) operating in non-contact mode at ambient conditions was used to confirm the uniformity of the film on the surface. The cantilever tip with a resonance frequency of 160–170 kHz and a typical spring constant of 40 N/m were obtained from Agilent-Molecular Imaging Corp.

Mass Spectrometry—A high resolution MALDI-TOF MS purchased from Agilent Technologies. with pulsed dynamic focusing was used to characterize the molecules on the substrate. MS analyses of the ions were detected in positive mode. The matrix, α -cyano-4-hydroxycinnamic acid (CHCA) (Sigma-Aldrich, >99.0% purity), was used without further purification and added in THF (10mg/mL). Samples for MALDI MS analysis were prepared by “dried-drop method”. A one microliter aliquot of the matrix solution was placed on each of the modified substrates and then dried at room temperature. The samples were then placed directly onto a MALDI sample plate using double sided tape and loaded into the MALDI-TOF. Analyte ionization was achieved by focusing a pulse of a laser light onto the sample/matrix preparation.

Results

Self assembled monolayers were formed on the native oxide surface of Stainless steel 316L and Nitinol alloys. X-ray photoelectron spectroscopy (XPS) analysis of the stainless steel 316L substrate was performed previously using a Phoibos 150 hemispherical energy analyzer and a monochromatized Al (1486.6 eV) source. Compositional results for the SS316L reference substrate were in reasonable agreement with the nominal SS316L bulk elemental composition⁵⁰ (Surface composition: Fe 66.01%, Cr 19.19 %, Ni 9.17 %, Mn 3.22% and Mo 2.42%). The Nitinol substrate's surface composition was 50% each of nickel and titanium oxides.^{45, 51} Thus, iron, chromium, nickel, manganese, molybdenum and titanium were used as the constituent metals for the alloys in this study. A long carbon chain of 18 was utilized as the standard to optimize van der Waals interactions and to prevent chain length variation from affecting the formation of ordered self assembled monolayers. The films formed were characterized by DRIFT spectroscopy after deposition, rinse in THF for 15 minutes and after sonication in THF for 15 minutes. In the spectra of the modified substrates, the C–H stretches of the methylene group are used as the reference peaks for alkyl chain organization in the SAM. 13, 52, 53 A spectra which contained $\nu_{\text{CH}_2 \text{ asym}} \leq 2918 \text{ cm}^{-1}$ and $\nu_{\text{CH}_2 \text{ sym}} \leq 2848 \text{ cm}^{-1}$ indicated that the alkyl chains in the film were ordered with the molecules organized in *all-trans* configuration on the substrate (Figure 1). The position of the peaks corresponding to $\nu_{\text{CH}_2 \text{ asym}}$ after rinsing with THF and after sonication in THF are provided in Table 2 for the acid- metal oxide and acid- alloy oxide systems. If the organic molecules were removed by rinse or sonication, the data is represented by dotted lines (----).

From Table 2, it is clear that phosphonic acid forms the most stable interaction with all of the substrates as the films remain intact after sonication on the metals and alloys. Sulfonic acid forms films on all of the surfaces and is stable to rinsing in solvent but only remains on SS316L after sonication. Carboxylic acid only formed films on SS316L and its major component Fe oxide and the films were stable on both surfaces.

Hydroxamic acid formed ordered films on more substrates than carboxylic acid. Previous reports on hydroxamic acid films indicated that they were more stable than carboxylic or phosphonic acid on metal oxides such as copper, aluminum and iron¹⁶ and had good corrosion inhibition efficiency due to their well-ordered alkyl chains and film formation.^{41, 54, 55} In this study, the hydroxamic acid films formed were stable to rinse but not to sonication, which was not performed in the previous report. To understand this result, AFM images of nitinol before and after the deposition and rinsing of the octadecylhydroxamic acid (ODHA) film is shown in Figure 2. The rms roughness of the control and modified substrates were compared. Modified surfaces with a similar rms roughness to the control surface are considered to be uniform films that follow the contour of the surface, while modified surfaces that have a much larger rms roughness than the control are multilayer or non-uniform films.^{36, 56} The rms roughness of the control and modified substrate were 14 Å and 75 Å, respectively (Figure 2). These values and the images clearly indicate that the surface is non-uniformly covered by multilayers and islands of agglomerates. These images are correlated to the contact angle values obtained of ODHA on nitinol which are lower than those expected for a hydrophobic surface as shown in Table 3. Moreover, the film was completely removed after sonication, and so it is concluded that the hydroxamic acid films are weakly bound, perhaps due in part to micelle formation seen in the images.

The films stable to rinse on the alloys and the major components of the alloy were further characterized by contact angle goniometry (Table 3). Contact angles can be a useful indicator of film quality and wettability of the surface when used in conjunction with other data. Contact angle values for the unmodified substrates were in the range of 50–60°. (Specific values are in the supplemental information). Here, the contact angles for phosphonic acid SAMs were the most hydrophobic. Sulfonic acid films produced lower contact angle values suggesting heterogeneous or incomplete surface films as can be seen in the AFM images of these substrates (AFM in supplemental information). For hydroxamic acid films on SS316L the standard deviations were high indicating that the films were not uniform on this surface. Contact angle values for films on nitinol, nickel and titanium were consistent with hydrophobic uniform films. Finally, carboxylic acid formed monolayers only on SS316L and iron and presented a hydrophobic interface on both of them indicating that the methyl tail group is presented at the interface.

The interaction between the organic moiety and the surface oxide can be characterized by DRIFT spectroscopy. This interaction can be either mono-, bi-, or tri-dentate and cases of each have been reported in the literature (Figure 3)^{17, 36, 37, 57}.

The bonding mode of the acid with the metals and alloys after sonication has been tabulated in Table 4 based on IR spectroscopy. For phosphonic acid SAMs the IR stretch values in the P-O region, which corresponds to 1300-950 cm⁻¹, provides valuable information about the type of bonding of the head group with the substrate. IR bands at 1227 cm⁻¹ and 950 cm⁻¹ are assigned to $\nu_{\text{P=O}}$ and $\nu_{\text{P-OH}}$ respectively and the peaks at 1074 cm⁻¹ and 1010 cm⁻¹ are assigned to the symmetric and asymmetric stretch of ν_{PO_3} .^{19, 20, 40} If the peak assigned to P-O and P=O stretches are observed, coupled with the disappearance of $\nu_{\text{P-O-H}} = 920 \text{ cm}^{-1}$, a bidentate coordination mode of the molecule to the surface is indicated.³⁷ This bonding mode was observed for stainless steel, nickel, titanium and iron oxides after each rinse and adhesion test. Some spectra of the modified iron substrates, however, were consistent with bidentate bonding modes while others were consistent with tridentate bonding. This is consistent with phosphonic acid SAMs on silicon oxide, where binding is tridentate.⁵⁸ The presence of $\nu_{\text{P=O}}$, $\nu_{\text{P-O}}$ and shifted $\nu_{\text{P-O-H}}$ indicates monodentate bonding³⁶ as observed for nitinol, molybdenum and manganese.

For carboxylic acids, the interaction of the head group with the substrate is correlated to the COO^- stretch frequency in infrared spectroscopy.⁵⁹ The IR spectrum of solid octadecylcarboxylic acid contains $\nu_{\text{C=O}}$ at 1700 cm^{-1} and $\nu_{\text{C-O}}$ at 1465 cm^{-1} .⁶⁰ Spectra of bound carboxylic acid with an absence of the carbonyl stretch ($\nu_{\text{C=O}}$) and the presence of the $\nu_{\text{COO}^- \text{asym}}$ peak around 1510 cm^{-1} and the $\nu_{\text{COO}^- \text{sym}}$ peak around 1400 cm^{-1} implies that the head group bonds to the surface through two oxygen atoms. This type of bidentate bonding is observed in silver or copper adlayers on gold⁶¹ and on air-exposed silver surfaces.⁶² For SAMs on aluminum and stainless steel, multiple carboxylate species have been observed.^{13, 34, 43} Here, a bidentate bonding of carboxylic acid with stainless steel was observed³² while the interaction on iron oxide was a mixture of monodentate and bidentate ($\nu_{\text{C=O}} = 1656\text{ cm}^{-1}$ and $\nu_{\text{COO}^- \text{sym}}$, $\nu_{\text{COO}^- \text{asym}}$ peak at $1470, 1580\text{ cm}^{-1}$, respectively).

The nature of the interaction between the hydroxamic acid molecule and the surface can be determined from the shifts and broadening of $\nu_{\text{C=O}}$, $\nu_{\text{N-O}}$, and $\nu_{\text{N-H}}$, indicating a change in head group bonding.^{16, 136} The CO and NH region of the ODHA solid contains $\nu_{\text{N-H}} = 3252$ and 1565 cm^{-1} , $\nu_{\text{C=O}} = 1660\text{ cm}^{-1}$, and $\nu_{\text{N-O}} = 1080\text{ cm}^{-1}$. The appearance of peak assigned to $\nu_{\text{C-O}}$ and the absence of $\nu_{\text{C=O}}$ peak coupled with a shift to lower frequency of the peak assigned to $\nu_{\text{N-H}}$ and $\nu_{\text{N-O}}$, represents a bidentate bonding with the substrate as observed on molybdenum samples (Figure 4A).

For sulfonic acid, the SO region of the ODSA solid shows $\nu_{\text{SOasym}} = 1178\text{ cm}^{-1}$, $\nu_{\text{SOasym}} = 1059\text{ cm}^{-1}$, $\nu_{\text{SOH}} = 946\text{ cm}^{-1}$ and $\nu_{\text{C-S}} = 794\text{ cm}^{-1}$. After deposition, rinsing and sonication on SS316L, the ODSA remains and the binding region indicates that there is a strong interaction between ODSA and SS316L due to the disappearance of the peak attributable to ν_{SOH} (946 cm^{-1} ; Figure 4B) and the broadening of the peaks attributable to S-O stretching indicating a bonding interaction between the oxygens and the surface.^{40, 63} Due to the changes in the spectra and the fact that the monolayer was not removed by rinse and sonication, a monodentate bonding interaction (and not a weaker hydrogen-bonding interaction) with SS316L is proposed.

To determine if the films remaining after sonication were monolayers or multilayers MALDI spectrometry was performed. Previous work in our group has shown that for monolayer films a peak for the mass of the sodiated monomer is seen in the mass spectrum and dimer peaks are not observed³⁶ (Figure 5). In the current study, for all films that were stable to sonication only the sodiated monomer peaks were observed in the mass spectrum. This indicates that the stable films were all monolayers.

Discussion

Other reports have postulated many possible reasons for the differences in film formation on metal oxides. The theories rely on a combination of organic and surface parameters such as oxide content of the alloy, organic moiety pKa, basicity of the surface,¹⁴ and hydroxyl content.^{14, 16, 35, 38, 64} In the two alloys studied here, the surfaces are composed of the oxides of the metals in similar ratios to the bulk alloy.^{4, 32, 37, 50, 65} Film formation, uniformity and stability on the surface could potentially be controlled by the most abundant metal oxide, the most reactive or the least reactive metal in the alloy. The results tabulated above do not pinpoint a controlling factor based on alloy content but clearly show that the presence of non-reactive metal oxides on the alloy surface will not prevent the formation of uniform, stable films, as in the case of SS316L.

For oxide substrates, formation of SAMs is often considered to be due to acid-base chemistry that occurs between the acid and the metal oxide substrate. In one proposed mechanism, the oxide, in the form of μ -oxo and hydroxyl groups, act as Lewis bases and are thus reactive under acidic conditions.^{13, 66} This reaction leads to the formation of a strong covalent bond

(Figure 6).¹³ An alternate mechanism is that proton transfer from the organic to the surface hydroxyls followed by dehydration leads to an ionic interaction between the deprotonated organic and the dehydrated surface (Figure 6).¹³

A notable difference between the acids under investigation was their head group acidity. The pKa of sulfonic acid is approximately 2.67 making it the strongest acid in this study, while phosphonic acids, have a pKa of 4.5.68⁶⁹ Two different surface pKa values are reported for the carboxylic acid deprotonation: a pKa value of 5 corresponds to COOH groups hydrogen-bonded to the interfacial water only, while a pKa of 9.5 corresponds to COOH headgroups hydrogen-bonded to each other as seen in organic solvent solutions.⁷⁰ In this study, the carboxylic acid is dissolved in THF. Hydroxamic acid (pKa = 9)^{16, 71–73} is stabilized by the resonance between the carbonyl and the hydroxyl group and therefore, hydroxamic acids tend to be more acidic than carboxylic acids.⁷² Thus, the pKa values of the head groups utilized in this study in increasing order is: sulfonic acid > phosphonic acid > hydroxamic acid > carboxylic acid. Therefore, if low organic molecule pKa facilitates film formation through an acid-base reaction, sulfonic acids should form films more easily on metal oxides than carboxylic acids.^{18, 31, 74–76}

Based on our observations, the ability to form films on the alloys and their substituents can be summarized as follows: Sulfonic acid = Phosphonic acid > Hydroxamic acid > Carboxylic acid. Therefore, films did form on the surface based on organic pKa. However, stability of the films was not strictly related to pKa. The most stable films on the largest number of substrates are formed by phosphonic acids. This is in agreement with literature data that phosphonic acids bind more strongly to metal oxides than other acids.^{18, 31, 74–76}

The proposed mechanisms in Figure 6 are a result of reports that metal oxides with higher hydroxyl contents, such as aluminum oxide, react with weaker acids such as carboxylic acids,^{13, 14, 16, 35, 77} while lower hydroxyl content surfaces, such as titanium dioxide, are considered to be less reactive, and therefore only react with very acidic molecules such as phosphonic acids.^{38, 78–81} The number of hydroxyl groups on the surface of the metal could affect the film formation by behaving as anchoring sites for the acid.^{14, 16, 35, 38, 64} Conversely, Lu et al observed that for Ti oxide surface, the formation of SAMs was not affected by surface hydroxyls.⁸² Based on literature reports, the effect of hydroxyl content on surface-organic interactions was analyzed (Table 5).^{16, 82–85} (The hydroxyl contents for the alloys were not reported in the literature in OH/nm².^{82, 86–88}) The hydroxyl content for the metal oxides were similar, except for molybdenum and titanium, which are lower. Although, the molybdenum oxide surface hydroxyl content was significantly lower than the others, films formed on this surface in the same manner as the other oxides and better than on nickel oxide. A range of values are reported for the hydroxyl content of titanium oxide and it only stably reacts with phosphonic acid. The hydroxyl contents for the alloy and metal systems in decreasing order are: Fe > Mn > Ni > Cr > Ti > Mo. This data does not predict the ability of the surfaces to form stable films with organic acids.

Previously, researchers correlated the reactivity of surfaces and organics with the isoelectric point (IEP) of the metal.^{16, 20, 89} Under this theory the pKa of the organic acid has to be lower than the IEP of the metal to be capable of forming ordered films on the metal oxide surfaces. Therefore, higher isoelectric points led to more reactive surfaces towards the acid, thus resulting in a stronger coordination when bound to the surface.¹⁴ Tao et al. observed that the formation of SAMs on silver, copper and aluminum oxide surfaces depended on the isoelectric point of the metal.¹⁴ The IEP of titanium (4–6), molybdenum (2.5), manganese(4), chromium(6.7), iron(7), and nickel(11) have been tabulated from literature reports in Table 5.^{83, 84, 90–92} The IEP of SS316L was previously calculated by XPS and reported to be 5.8 whereas a more recent work using potentiometric titrations by Takahashi⁹³ reported the IEP of

stainless steel 316L to be 8.5. The IEP of nitinol alloy is unknown because one would need a salt of the alloy, which is not available.^{83, 84}

Utilizing the idea that the IEP was a major controlling factor in film formation, sulfonic and phosphonic acid are the only acids capable of forming strong and stable interactions on iron, chromium, manganese, SS316L and titanium oxide surface where as the nickel oxide surface can theoretically be modified using carboxylic, hydroxamic, sulfonic and/or phosphonic acids. In contrast, our observations show that phosphonic acid reacts with all the metals and alloys and remains attached even after sonication as predicted. However, while sulfonic acid interacts with most oxides the interaction is not strong and is removed by sonication. Carboxylic acid reacts stably with iron and stainless steel oxides to form ordered films but not with nickel oxide which was predicted by the IEP rule. This data indicates that the IEP of a surface may be a good predictor for the formation of films on surfaces, but it is not the controlling factor and other parameters play a role.

Conclusions

From this study, it is clear that film formation on alloy oxides is related to several factors, including the reactivity of the metals that compose the surface. However, the nonreactive components of the alloy do not prevent complete film formation. Therefore, the reactive metal sites may act as nucleation sites for film formation on the alloys. For both alloys and their constituent metals, decreasing pKa of the organic moiety and a higher isoelectric point of the surface generally leads to film *formation*. However, the film *stability* is not necessarily related to these factors. Further experiments into the role of these and other parameters such as surface roughness, grain boundaries in alloys, electron affinity and ionization potential by both experimental and computational studies are needed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

DRIFT spectra of the C-H stretching region of octadecylsulfonic acid film on Mn after rinse (bottom) and sonication (top). The film is removed by sonication. The $\nu_{\text{CH}_2 \text{ asym}} = 2914 \text{ cm}^{-1}$ and $\nu_{\text{CH}_2 \text{ sym}} = 2848 \text{ cm}^{-1}$.

Figure 2.

(a) AFM topography image of clean NiTi (rms roughness= $14 \text{ \AA}$), (b) AFM image of NiTi surface after modification with ODHA and rinsed with THF (rms roughness= $75 \text{ \AA}$) in topography and amplitude

Figure 3.
Monodentate, bidentate and tridentate bonding of phosphonic acid on stainless steel 316L.

A.

B.

Figure 4.

A. IR spectra of molybdenum modified with ODHA showing bidentate bonding with peaks centered at 1314 (ν_{CO}), 1444 and 1556 cm^{-1} (ν_{COO^-} $_{\text{symm}}$, ν_{COO^-} $_{\text{asymm}}$ respectively) and 1346 cm^{-1} for ($\nu_{\text{C-N}}$). B. IR spectrum of SS316L modified with ODSA with peaks centered at $\nu_{\text{SOasym}} = 1174 \text{ cm}^{-1}$, $\nu_{\text{SOsym}} = 1068 \text{ cm}^{-1}$ and $\nu_{\text{C-S}} = 798 \text{ cm}^{-1}$.

Figure 5. MALDI spectra of monolayer film of octadecylhydroxamic acid sodiated on titanium m/z 322.017 amu (ODHA + Na⁺). Dimer peak is not observed at 621 amu.

Figure 6. Proposed binding schemes for organic acids on metal oxide surfaces. Left: Covalent Right: Ionic using carboxylic acids on SS316L.

Table 1

Procedure numbers used for each acid/ metal combination.

ACIDS	Sulfonic Acid	Phosphonic acid	Hydroxamic acid	Carboxylic acid
<i>Metals</i>				
SS316L	6	4	9	7
Nitinol	2	1	3	3
Nickel	2	1	9	8
Titanium	2	1	3	3
Iron	6	4	9	8
Chromium	6	4	9	8
Molybdenum	6	5	9	8
Manganese	6	4	9	8

Table 2

CH₂ asym stretching frequency for each oxide-acid combination in the study. Rinse= Rinse in THF; Sonic= Sonication in THF.

	Sulfonic acid V _{CH2 asym} (cm ⁻¹)		Phosphonic acid V _{CH2 asym} (cm ⁻¹)		Hydroxamic acid V _{CH2 asym} (cm ⁻¹)		Carboxylic acid V _{CH2 asym} (cm ⁻¹)	
	Rinse	Sonic	Rinse	Sonic	Rinse	Sonic	Rinse	Sonic
SS 316L	2913	2916	2912	2911	2916	----	2915	2917
Nitinol	2915	----	2914	2913	2915	----	----	----
Nickel	2918	----	2914	2915	2916	----	----	----
Titanium	2916	----	2913	2913	2915	----	----	----
Iron	2916	----	2915	2916	----	----	2915	2915
Chromium	2915	----	2914	2914	----	----	----	----
Molybdenum	2914	----	2914	2914	2913	2913	----	----
Manganese	2914	----	2914	2914	2914	----	----	----

Table 3

Static contact angle data for rinsed organic films on metals and alloy oxides

ACIDS	Sulfonic acid		Phosphonic acid		Hydroxamic acid		Carboxylic acid	
	θ°	$\pm$ <i>Stdev</i>	θ°	$\pm$ <i>Stdev</i>	θ°	$\pm$ <i>Stdev</i>	θ°	$\pm$ <i>Stdev</i>
<i>Oxide</i>								
SS 316L	90	4	108	3	76	9	104	1
Nitinol	89	8	107	3	103	3	----	----
Nickel	93	8	109	5	100	4	----	----
Titanium	82	18	96	5	101	3	----	----
Iron	83	10	98	4	----	----	87	5

Table 4

Proposed bonding motif of organic films after sonication; monodentate, bidentate, tridentate or hydrogen bonding with substrate.

ACIDS	Sulfonic acid	Phosphonic acid	Hydroxamic acid	Carboxylic acid
<i>Metals</i>				
SS316L	Mono	Bi	----	Bi
Nitinol	----	Mono	----	----
Nickel	----	Bi	----	----
Titanium	----	Bi	----	----
Iron	----	Bi/ Tri	-----	Mono
Chromium	----	Mono or H	-----	----
Molybdenum	-----	Mono	Bi	----
Manganese	----	Mono	----	-----

Table 5

Isoelectric points reported previously and hydroxyl content for the metals and alloys

Metals	Isoelectric point	Hydroxyl content (OH / nm ²)
SS 316L	5.8, 8.5	–
Nitinol	Not reported	–
Nickel	11	14–15
Titanium	4–6	7–12.5
Iron	7	15
Chromium	6.7	13
Molybdenum	2.5	2.4–2.7
Manganese	4	14.5