Langmuir **2001,** *17,* 5736−5738

Self-Assembly and Bonding of Alkanephosphonic Acids on the Native Oxide Surface of Titanium

Ellen S. Gawalt, Michael J. Avaltroni, Norbert Koch, and Jeffrey Schwartz*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544-1009

Received May 2, 2001. In Final Form: July 17, 2001

Alkanephosphonic acids assemble from solution on the native oxide surface of titanium to form alkane chain ordered films which, however, are easily removed by solvent rinse. In contrast, assembling the alkanephosphonic acid from solution on the native oxide surface of titanium followed by gentle heating gives an alkane chain ordered film of the acid which is strongly surface-bound; this film resists removal by solvent washing or simple mechanical peel testing. Surface imaging by atomic force microscopy shows comprehensive surface coverage by aggregated islands, with elevations of each consistent with monolayer formation. ω-Carboxyalkanephosphonic acids are also easily bound to the native oxide surface of Ti through self-assembly/heating. Infrared analysis is consistent with surface attachment through the phosphonate headgroup.

Lightweight, strong titanium metal is of increasing importance in fields as diverse as aviation and aerospace,[1] high-performance sports equipment,[2] and medical implants.[3−5] Titanium metal readily surface oxidizes,[6] but the native oxide coating is generally resistant to further chemical reaction, which makes coating with organics problematic. Alkanephosphonic acids are common coatings[7] for native oxide surfaces of metals or alloys such as tin,[8,9] iron,[10] steel,[7,11] aluminum,[10−12] or copper[11] or for bulk oxides such as mica.[13] Indeed, alkanephosphonic acids can react under ambient conditions with mica[13] or the native oxide surfaces of iron,[10] copper,[14] or aluminum[10] to give adhered, alkane chain ordered films. In marked contrast, surface modification of the native oxide surface of titanium with these acids can be problematic. Indeed, even though phosphonic acids react strongly with ZrO_2 from hot solution, comparable reaction with TiO_2 is poor.[15] We now report that self-assembly of alkanephosphonates on the native oxide surface of Ti can be effected by a simple procedure of aerosol deposition followed by solvent evaporation; subsequent warming gives a strongly surface-bound, ordered film of the alkanephosphonate species which resists removal by solvent washing or mechanical "peel" testing.

Squares of titanium foil (1 cm × 1 cm; 0.25 mm thickness; 99.6%; Goodfellow, Inc.) were sanded, rinsed with hot methanol, and stored at 160 °C in air, which gives a surface coating of hydroxylated titanium dioxide.[6] A solution of octadecylphosphonic acid in dry tetrahydrofuran (0.75 mM) was aerosol sprayed (using a TLC sprayer and N_2) onto these Ti squares. Evaporation of the solvent under ambient conditions and analysis by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) showed octadecylphosphonic acid on the surface, with peaks recorded at 2914 cm^{-1} ($\nu_{asymmCH_2}$) and 2846 cm^{-1} (ν_{symmCH_2}). Frequencies for methylene group stretching modes are cited to be diagnostic of alkyl chain order in oxide surface adsorbed organics:[15−19] if $\nu_{asymmCH_2} = 2918\ cm^{-1}$, chains are deemed to be "ordered," or in a "crystalline" state, with CH_2 groups staggered in all-trans configurations; if $\nu_{asymmCH_2} = 2922\ cm^{-1}$, these chains are considered to "disordered," or in a "liquidlike" film.[15−19] On the basis of this criterion, the alkyl chains of the surface-adsorbed octadecylphosphonic acid are ordered. However, adhesion of this film to the Ti native oxide surface is weak; the acid can be removed by simple solvent rinse, as ascertained by IR (Figure 1).

A strongly surface-bound film of alkanephosphonate can be formed on the Ti native oxide surface by heating the material prepared as described above (but before rinsing) at 120 °C for 18 h. Immersion of treated Ti samples in dry THF twice, for 5 min each, removed physisorbed phosphonic acid. Samples were then dried (room temperature, 0.1 Torr) and analyzed by DRIFT, which showed that octadecylphosphonate remained on the surface. A peel test (Scotch tape no. 234; adhesive strength to steel 37 oz/in.) was next performed by pressing the tape down firmly on the treated surface and then quickly removing it. Again, IR analysis showed the persistence of the surface octadecylphosphonate; CH_2 stretching modes were recorded at 2914 and 2946 cm^{-1}, indicative of alkyl chain ordering.[15−19] Some reduction in CH_2 stretching mode peak intensity was measured between initial aerosol deposition and final washing and peeling away of physisorbed

---

(1) Chattopadhyay, A. A.; Zentner, M. R. *Aerospace and Aircraft Coatings*; Federation of Societies for Coatings Technology: Philadelphia, 1990.

(2) Froes, F. H. *JOM* **1997**, *49*, 15.

(3) Geissler, U.; Hempel, U.; Wolf, C.; Scharnweber, D.; Worch, H.; Wenzel, K.-W. *J. Biol. Mater. Res.* **2000**, *51*, 753.

(4) Oji, M. O.; Wood, J. V.; Downes, S. *J. Mater. Sci.: Mater. Med.* **1999**, *10*, 869.

(5) Anselme, K.; Linez, P.; Bigerelle, M.; Le Maguer, D.; Le Maguer, A.; Hardouin, P.; Hildebrand, H. F.; Iost, A.; Leroy, J. M. *Biomaterials* **2000**, *21*, 1567.

(6) Lu, G.; Bernasek, S. L.; Schwartz, J. *Surf. Sci.* **2000**, *458*, 80.

(7) Fang, J. L.; Wu, N. J.; Wang, Z. W.; Li, Y. *Corrosion* **1991**, *47*, 169.

(8) Hibi, T.; Morikawa, H.; Yamamoto, K.; Ikeda, J.; Tatsumi, K. In *Chem. Abstr.*; Daido Chemical Industry Co. Ltd.: Japan, 1992; Vol. 116, 109915s.

(9) Kuznetsov, Y. I.; Raskol'nikov, A. F. *Prot. Met.* **1992**, *28*, 545.

(10) Gawalt, E. S.; Lu, G.; Bernasek, S. L.; Schwartz, J. *Langmuir* **1999**, *15*, 8929.

(11) Van Alsten, J. G. *Langmuir* **1999**, *15*, 7605.

(12) Nitowski, G. A.; Wiserman, L. F.; Wefers, K. In *Chem. Abstr.*; Aluminum Co. of America: US, 1994; Vol. 121, 20979w.

(13) Woodward, J. T.; Schwartz, D. K. *J. Am. Chem. Soc.* **1996**, *118*, 7861.

(14) Gawalt, E. S. Unpublished results.

(15) Gao, W.; Dickinson, L.; Grozinger, C.; Morin, F. G.; Reven, L. *Langmuir* **1996**, *12*, 6429.

(16) Schilling, M. L.; Katz, H. E.; Stein, S. M.; Shane, S. F.; Wilson, W. L.; Buratto, S.; Ungashe, S. B.; Taylor, G. N.; Putvinski, T. M.; Chidsey, C. E. D. *Langmuir* **1993**, *9*, 2156.

(17) Sondag, A. H. M.; Raas, M. C. *J. Chem. Phys.* **1989**, *91*, 4926.

(18) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

(19) Byrd, H.; Pike, J. K.; Talham, D. R. *Chem. Mater.* **1993**, *5*, 709.

10.1021/la010649x CCC: $20.00

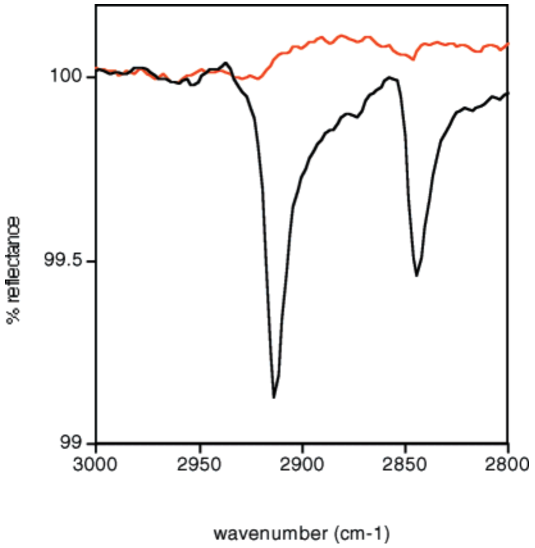

Figure 1. IR spectra of a deposited film of octadecylphosphonic acid (no heat, control), before (lower trace) and after solvent wash (upper trace).

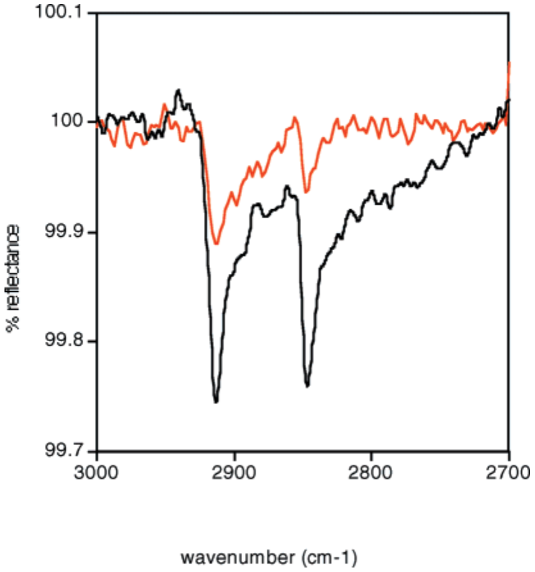

Figure 2. IR spectrum of a film of octadecylphosphonic acid formed from six cycles of deposition, with heat treatment (lower trace), compared with one cycle (upper trace), after both solvent wash and tape peel tests.

material. Surface coverage of chemisorbed octadecylphosphonate could be enhanced through repeated sequences of aerosol dosing (0.75 mM phosphonic acid in THF), heating (120°, 18 h), and rinsing with THF. (Similar film growth through repeated treatment has been found for an alkanephosphonic acid on mica.[13]) Coverage was monitored after each sequence by IR, which appeared to asymptote after six cycles of dose/heat/rinse: IR analysis following rinsing and tape peeling showed an approximately 5-fold increase in surface coverage versus one cycle (Figure 2); alkyl chains were still ordered by the IR criterion.

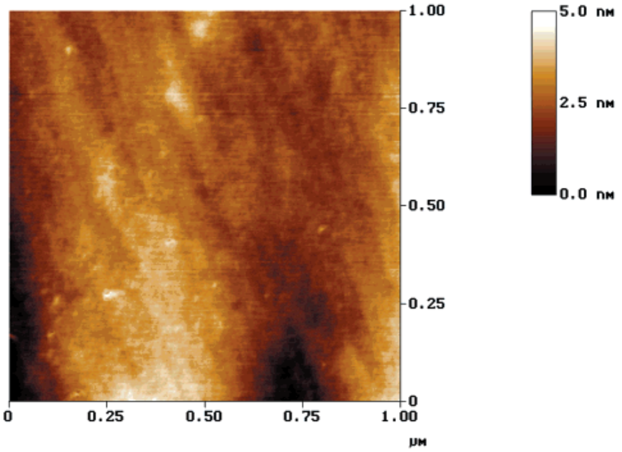

Figure 3. AFM micrograph analysis of the polished Ti surface before reaction with octadecylphosphonic acid.

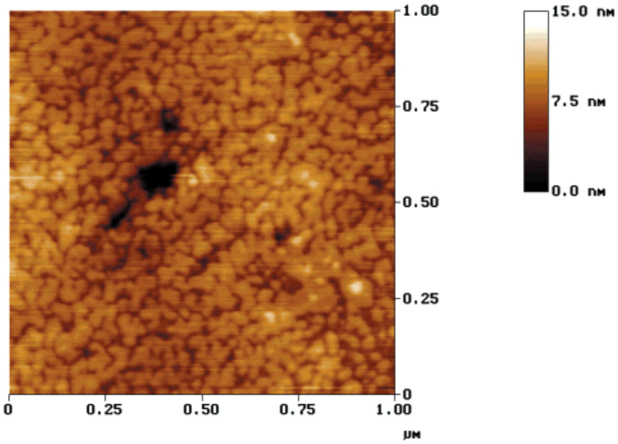

Figure 4. AFM micrograph analysis of the polished Ti surface after reaction with octadecylphosphonic acid.

A self-assembled film of octadecylphosphonic acid on the native oxide surface of polished Ti foil was prepared by six cycles of spray−heat−rinse and was studied by atomic force microscopy (AFM) using a Dimension 3000 (Digital Instruments) operated in “soft” TappingMode. An AFM micrograph of the polished Ti foil surface shows it to have grooves (resulting from the polishing process), but regions between these grooves are appreciably flat (mean roughness, ≈0.7 nm; Figure 3). Section analyses examined surface roughness in more detail. The morphology of the surface changed dramatically on formation of the octadecylphosphonic acid film. Here, AFM micrograph (Figure 4) and section analysis showed islands (typical diameter, ≈50 nm) of similar height (≈2.2 nm), consistent with monolayer formation on the surface, and the mean roughness of the surface increased to 1.5 nm on monolayer attachment. With reference to film height data obtained for a self-assembled monolayer of this same phosphonic acid on mica (≈1.8 nm),[13] an alkyl chain tilt angle of ca. 33° can be estimated for our system.

The spray/heat method for effecting chemisorption can also be used with functionalized alkanephosphonic acids. In typical procedures, cleaned and ambient condition oxidized titanium foils were treated with aerosol sprays of either 4-phosphonobutyric acid or 2-phosphonopropanoic acid in doubly distilled water. Samples were heated to 120° for 18 h and were then analyzed by DRIFT. Strong peaks for ν_{CO} at 1690 cm^{-1} (4-phosphonobutyric) and 1700 cm^{-1} (2-phosphonopropanoic) showed the presence of surface-uncoordinated hydrogen-bonded carboxylic acid groups,[20,21] indicating preferential attachment of the phosphonic acid group to the surface.[20,21] Aqueous wash and Scotch tape peel tests were done, and the persistence of the acid on the Ti native oxide surface was confirmed by IR analysis (Figure 5).

---

(20) Duevel, R. V.; Corn, R. M. *Anal. Chem.* **1992**, *64*, 337.

(21) Pawsey, S.; Yach, K.; Halla, J.; Reven, L. *Langmuir* **2000**, *16*, 3294.

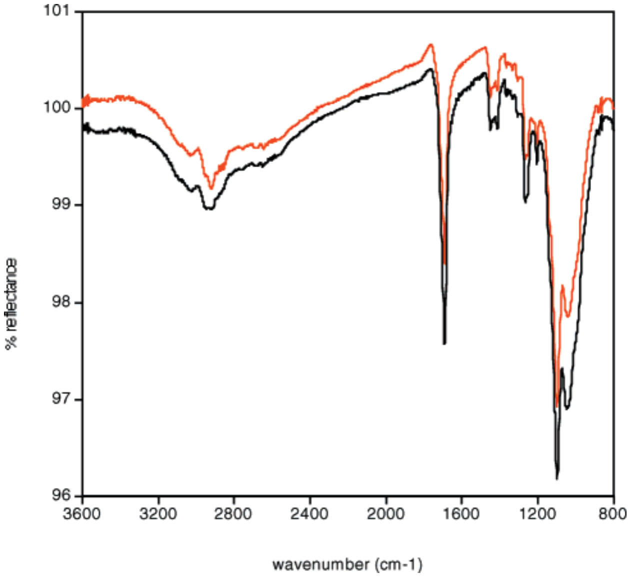

Figure 5. IR spectra of a film of 4-phosphonobutyric acid formed from one cycle of deposition, with heat treatment, before (lower trace) and after both solvent wash and tape peel tests (upper trace).

It seems that ordered films of phosphonic acids can assemble on the titanium native oxide surface, perhaps through hydrogen-bonding interactions among phosphonic acid headgroups and van der Waals interactions of methylene units, in a manner reminiscent of the formation of phospholipid monolayers on hydrophilic surfaces.[22] Even though this film is weakly bound to the surface, the headgroups may be organized at the organic−oxide interface; thermally driven subsequent attack on the native oxide versus simple desorption might be facilitated by cooperative behavior of these headgroups. That film surface coverage can be increased by successive treatments with the alkanephosphonic acid suggests that chemisorbed nucleation sites can assist in surface attack. Also, the observation that ω-carboxylic acid substitution gives rise to high surface coverage, even with only one "cycle" of spray−heat, is consistent with a model in which such functionality can enhance organization of the phosphonic acid on the oxide surface through "tailgroup" hydrogen-bonding networks. Studies of oxide−phosphonate interfacial structure and formation with variously substituted phosphonic acids are now under way.

Acknowledgment. The authors thank The Seaver Institute, the National Institutes of Health, and the Lord Corporation for support of this research. They also thank B. S. Nemetski (Department of Mechanical and Aerospace Engineering, Princeton University) for assistance with AFM imaging and Dr. E. Barry Troughton (Lord Corporation) for critical commentary.

Supporting Information Available: AFM section analyses of polished Ti before and after reaction with octadecylphosphonic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

LA010649X

---

[22] Cevc, G.; Seddon, J. M. In *Phospholipids Handbook*; Cevc, G., Ed.; Marcel Dekker: New York, 1993.