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Enhanced Bonding of Organometallics to Titanium via a Titanium(III) Phosphate Interface

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Titanium metal combines the strength of steel with the light weight of aluminum, which explains in part its appeal in the aviation and aerospace industries,[1] high-performance sports equipment,[2] and medical implant and replacement devices.[3−5] Titanium is resistant to corrosion under ambient conditions, which also makes it attractive as an architectural material:[6] exposure of a clean surface of titanium metal or its alloys to oxygen results in the spontaneous formation of a layer of titanium oxides;[7−10] titanium dioxide is uppermost in this layer[10] and protects the metal against further chemical attack.[7] Rapid titanium corrosion can occur, however, when this protective TiO_2 layer is dissolved and its reformation is inhibited.[7] Indeed, reducing acids (e.g., hydrobromic, sulfuric, and phosphoric) attack Ti or its alloys under various conditions of heat and acid concentration, especially with exclusion of oxidizing agents including air.[7] For example, Ti metal rapidly dissolves in 85% phosphoric acid at 80−100 °C to give a purple solution; titanium(III) dihydrogen orthophosphate ($Ti[H_2PO_4]$, **1**, "TiP") can be isolated from this solution as gray-purple crystals.[11] We find that when a film of aqueous phosphoric acid on air-oxidized Ti foil is heated, a layer of crystalline TiP is formed which appears to be strongly adhered to the surface (as **1/Ti**). Crystallographic analysis[11] of **1** shows a hexagonal, layered structure similar to that of the scandium analogue, in which phosphate hydroxyl groups lie above and below the layers in a titanium phosphate polymer.[11] Accordingly, protolytically labile organometallics react with a higher deposition yield on **1/Ti** than on the native oxide layer of Ti; the resulting surface-bound complexes can be further elaborated by reaction of coordinated ligands with various organics.[12−15] Thus, **1/Ti** might be considered to be an attractive interfacial alternative to chromates[1] for adhesion enhancement of organics to Ti.

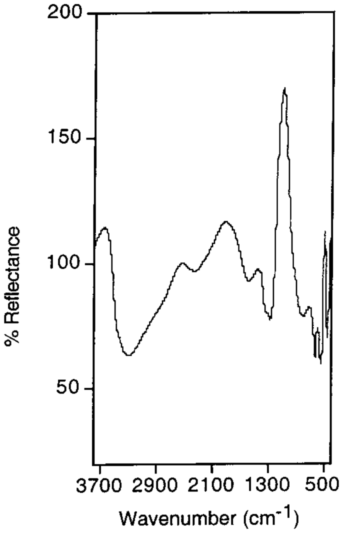

Figure 1. DRIFT spectrum of **1/Ti** (TiP).

Experimental Section

General. Titanium foil (0.25 mm thick; 99.6%, Goodfellow, Inc.) was sanded first with 250 grit and then with 600 grit SiC paper, then cleaned with hot methanol, cut into 1 cm × 1 cm samples, and stored in an oven at 200 °C. Octadecyltriethoxysilane (**2**; 95%, Gelest) was used as received. Tetra(*tert*- butoxy)zirconium (**3**, Aldrich) was distilled in vacuo and stored under N_2. Aerosol treatment of samples with solutions of **2** or octadecylphosphonic acid (**4**) was done in a simple glovebox under N_2 flow using a sprayer (Supelco) designed for use in thin-layer chromatography. "Peel" tests were done by pressing a strip of Scotch masking tape no. 234 (37 oz/in. adhesion to steel) onto a substrate and then rapidly peeling the tape off. X-ray powder diffraction (XRD) was performed using a Rigaku Miniflex spectrometer with Cu Kα radiation and a Zn filter. Data were collected from 8 to 55° 2Θ and were analyzed and refined using Jade 3.0 Pattern Processing for Windows.

Titanium(III) Dihydrogen Orthophosphate on Titanium (1/Ti, TiP). Titanium foils were dipped in an aqueous solution of phosphoric acid (1.45 M, pH 1.5) for 1 h at ambient temperature and pressure; foils were then removed from solution and warmed in an oven at 120 °C for 18 h. Samples were then cooled, rinsed with water, and peeled with masking tape to remove any weakly adsorbed material. X-ray powder diffraction analysis was performed following rinsing and peeling. Diffuse reflectance Fourier transform infrared analysis (DRIFT) showed strong OH group absorption (Figure 1).

$[Ti]-[TiP]-[O]_x-Zr(t\text{-}OBu)_{4-x}$. Foils of **1/Ti** and ambient-oxidized Ti (controls) were put in a horizontal tube which could be externally cooled and which was equipped with two stopcocks for exposure to vacuum (10^{-3} Torr) or to vapor of tetra(*tert*-butoxy)zirconium (**3**). Foils were subjected to three cycles each consisting of alternating exposure to vapor of **3** with external evacuation for 15 min, followed by 30 min exposure to the organometallic without external evacuation. The first cycle was done at room temperature, and the latter two with external cooling by dry ice. Foils were then evacuated at room temperature (10^{-3} Torr) for 16 h to remove any physisorbed **3**. DRIFT analysis confirmed formation of surface Zr alkoxide.[12]

$[Ti]-[TiP]-[O]_x-Zr(O_3PC_{18}H_{37})_{4-x}$. Foils coated with $[Ti]-[TiP]-[O]_x-Zr(t\text{-}OBu)_{4-x}$ were sprayed with a 0.75 mM solution of octadecylphosphonic acid (**4**) in dry tetrahydrofuran. Samples were evacuated overnight (0.1 Torr), rinsed, peeled, and analyzed by DRIFT.[12]

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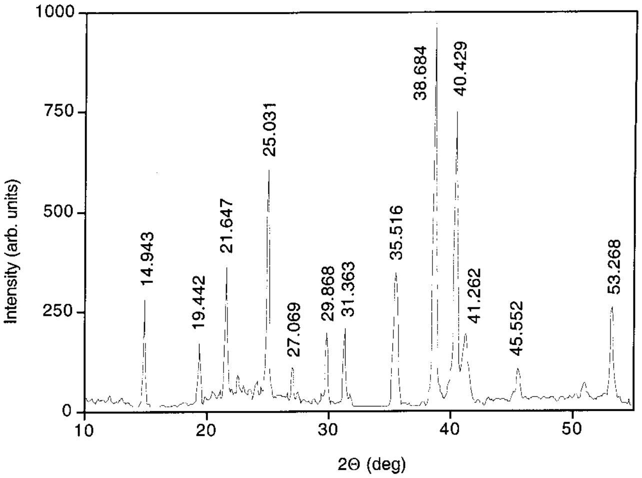

Figure 2. XRD pattern for **1/Ti** prepared from phosphoric acid on Ti foil.

[Ti]−[TiP]−[O]−Si(OC$_2$H$_5$)$_x$(C$_{18}$H$_{37}$). Foils of **1/Ti** and ambient-oxidized Ti (controls) were aerosol sprayed with a 0.8 mM THF solution of octadecyltriethoxysilane, heated at 120 °C for 24 h, rinsed, peeled, and analyzed by DRIFT.

Results and Discussion

A sample of Ti foil was sanded, cleaned with methanol, dried, and placed in a stirred, aqueous solution of phosphoric acid (1.4 M, 8.5%) for 1 h at room temperature in air. The air-oxidized foil was removed from the acid bath, leaving a thin film of the aqueous acid on its surface. The foil was then warmed in an oven at 120° for 18 h, cooled to room temperature, and analyzed by XRD, which showed two different titanium phosphate species on its surface. One component, $Ti_4H_{11}(PO_4)_9 \cdot H_2O$,[16,17] could be easily removed by rinsing with water, but the other, **1/Ti**, remained on the surface. Indeed, XRD analysis of the rinsed foil, which had a dull purplish-gray color, showed peaks only for **1** (which were identical to those of powdered **1**[11,18]) and for the Ti metal substrate.[19,20] There is no long-range order to **1/Ti**; imaging of both the starting Ti metal and **1/Ti** by profilometry (at 5 mm/s with 5 mg force) showed rather rough surfaces. In an imaged area ($100\mu \times 100\mu$), the overlayer of TiP varied up to 3μ above the mean, and uneven surface structures were readily apparent. The resistance of **1** to removal from Ti by rinsing or peeling with Scotch tape was verified by XRD analysis; little change in relative intensities of XRD peaks for **1** and the Ti substrate were measured before and after these tests (Figure 2). Since there is no preferred orientation for **1** on the Ti substrate, phosphate group derived hydroxyls of **1** are likely also randomly oriented.

Although attachment of organic films to oxide surfaces commonly utilizes carboxylic[21−23] or phosphonic acid[24] "headgroups", neither class of these organics adheres strongly to **1/Ti**. For example, **1/Ti** was treated with an aerosol solution of stearic acid (0.8 mM in THF) and then was evacuated at 0.1 Torr; IR analysis showed the presence of surface-adsorbed acid which was, however, easily removed by solvent rinse. A similar observation was made for **4**. Also, **1/Ti** treated with vapor of stearic acid through several cycles of exposure and evacuation as described above for **3** (but with the reservoir of stearic acid heated to 120 °C) showed no net stearic acid on the surface by DRIFT analysis. It may be that in contrast to surface−overlayer interactions involving metallic oxides and organic acids (where proton transfer might occur from the organic to the surface), chemisorption on **1/Ti** occurs by proton transfer from the relatively acidic surface OH groups to the organic overlayer. Indeed, octadecylamine adheres well to **1/Ti** when deposited either from the vapor phase or solution, but organic acids might not be easily protonated, themselves, under our deposition conditions.

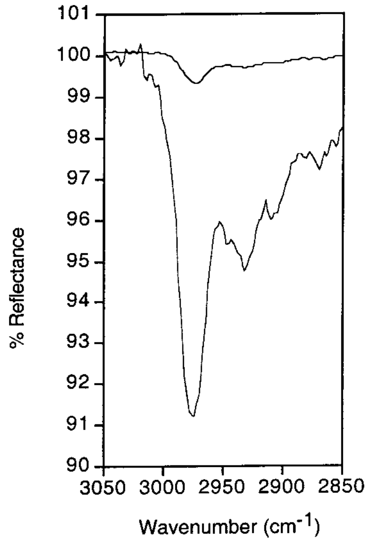

Figure 3. DRIFT spectra of **3** deposited on **1/Ti** by vapor phase deposition following rinse and peel (lower) and a control on the Ti metal native oxide (upper).

The hydroxyl groups of **1/Ti** can also serve as reactive sites for covalent attachment of protolytically labile reagents, such as Zr[12,25] or Si[14,15] alkoxides; surface loadings of these organometallics are far higher than those obtained on the native oxide of Ti in which only about 15% of surface oxygen is derived from hydroxyl groups.[10] For example, deposition of **3** onto the Ti native oxide surface[25] gives [Ti]−[O]−Zr(*t*-OBu)$_3$ which has a characteristic peak ($\Delta R/R \approx 0.75\%$) at 2977 cm^{-1} in the IR ($\nu_{CH_3\ antisym}$). In comparison, reaction of **3** with **1/Ti** also gives product with a peak at 2977 cm^{-1}, but which is about 10-fold stronger ($\Delta R/R \approx 10\%$). Since it has been established[25] that **3** reacts with hydroxylated surfaces by proton transfer, this increase in peak intensity is consistent with an increase in the surface content of reactive OH sites for **1/Ti** versus the Ti native oxide [Figure 3].

Surface-bound [Ti]−[O]−Zr(*t*-OBu)$_3$ has been shown to be an effective interface between alkanephosphonic acids and the Ti native oxide surface, for example, by ligand exchange with **4** to give [Ti]−[O]−Zr(*t*-OBu)(O$_3$PC$_{18}$H$_{37}$)$_2$[12] which has a characteristic IR peak at 2923 cm^{-1} (ν_{asymCH_2}, $\Delta R/R \approx 0.4\%$). DRIFT analysis following reaction of **4** (as a 0.75 mM solution in THF) with [Ti]−[TiP]−[O]$_x$−Zr(*t*-OBu)$_{4-x}$, rinsing, and peeling showed a characteristic long alkyl disordered-chain pattern[23] with peaks at 2853 cm^{-1} (ν_{symCH_2}) and 2953 cm^{-1} (ν_{asymCH_3}), as well as at 2923 cm^{-1} (ν_{asymCH_2}), but with a greater loading of surface Zr complex

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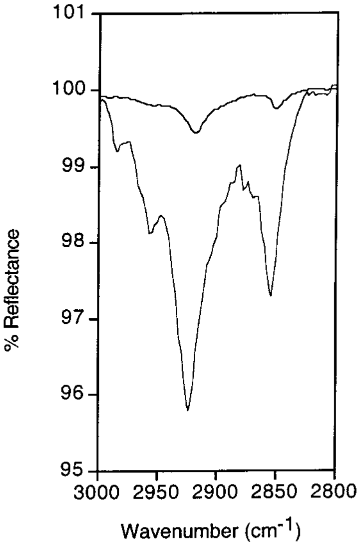

Figure 4. DRIFT spectra of **4** deposited on [Ti]−[TiP]−[O]$_x$−Zr(t-OBu)$_{4-x}$ by vapor phase deposition following rinse and peel (lower) and a control on [Ti]−[O]−Zr(t-OBu)$_3$ (upper).

on **1/Ti** ($\Delta R/R \approx 2\%$) [Figure 4] than on the Ti native oxide surface. Water wetting contact angle measurements gave values of 112° ± 2° for [Ti]−[TiP]−[O]$_x$−Zr(O$_3$PC$_{18}$H$_{37}$)$_{4-x}$ versus 54° for the Ti native oxide and 31° for **1/Ti**, consistent with a comprehensive hydrophobic surface coating of [Ti]−[TiP]−[O]$_x$−Zr(O$_3$PC$_{18}$H$_{37}$)$_{4-x}$. Disordered alkyl chains in the complex overlayer may derive from the roughness of the surface of **1/Ti**.

Silanes are reagents commonly used to couple functionalized organics to a variety of hydroxylated surfaces.[26,27] Loading of silanes on the native oxide of Ti can be light,[14,15] presumably due to its low surface OH group content.[10] We find that octadecyltriethoxysilane (**2**) reacts irreversibly with **1/Ti** but not with the Ti native oxide surface under comparable conditions. For example, a 0.8 mM THF solution of **2** was aerosol sprayed onto both Ti and **1/Ti** foils which were then heated in a 120 °C oven for 24 h. Foils were then analyzed by DRIFT following rinsing and peeling (Figure 5). Chemisorbed **2** was easily discernible on treated TiP-covered samples, with peaks at 2850 cm^{-1} ($\nu_{\mathrm{sym\ CH_2}}$) and 2924 cm^{-1} ($\nu_{\mathrm{asymm\ CH_2}}$), characteristic of disordered alkyl chains. In contrast, no **2** could be detected on the Ti native oxide surface control, either after heating at 120 °C or evacuation at 0.1 Torr.

Conclusions

A layer of Ti(III) phosphate can be formed on the native oxide surface of Ti metal by film formation and heating.

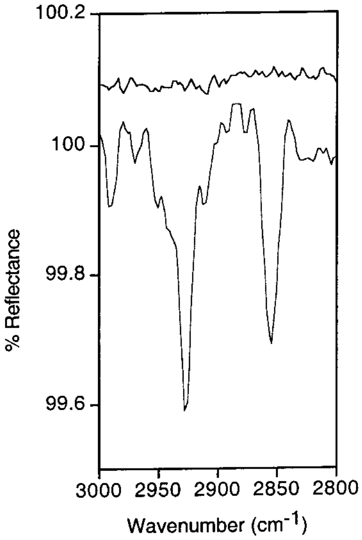

Figure 5. DRIFT spectra of **2** deposited on **1/Ti** by vapor phase deposition following rinse and peel (lower) and a control on the Ti metal native oxide (upper).

This surface compound, Ti(III) dihydrogen orthophosphate (TiP), effectively interfaces the Ti native oxide (as **1/Ti**) and surface derivatization reagents, such as alkoxyalkylsilanes and Zr alkoxides. The surface Zr alkoxides can, in turn, act as surface linking reagents with alkylphosphonic acids, which gives surface-bound Zr phosphonates. Because of the high degree of surface hydroxylation of Ti(III) dihydrogen orthophosphate compared with the native oxide layer of Ti, deposition loadings of the alkoxyalkylsilanes, Zr alkoxides, and Zr phosphonates are far higher on **1/Ti** than on the native oxide. Long alkyl chain substitutes bound through reactive headgroups to TiP are apparently disordered (by IR) but are strongly adhered to it. Disorder of these chains is not unexpected, given the surface roughness of the TiP layer. Elaboration chemistry of functionalized silane and phosphonate derivatives on TiP is now under investigation.

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