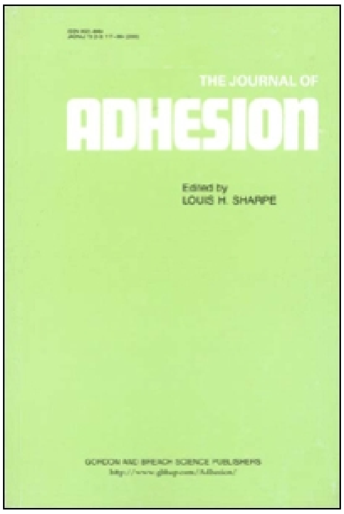

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Spectroscopic Characterization of Acidity of Titanium (6%, Al-4%, V) Surfaces†

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Acid-base characteristics of titania powders and of Ti 6-4 metal coupons after pretreatment by the Turco 5578 and phosphate-fluoride processes have been studied. Color changes of indicators spread from solution on the metal surface were detected using diffuse reflectance visible spectroscopy (DRVS). The Turco etched Ti 6-4 surface was found to be basic while the phosphate-fluoride etched Ti 6-4 surface was acidic. Effects due to the experimental conditions of time, solvent, and temperature were also examined. ESCA (electron spectroscopy for chemical analysis) was done to determine if shifts in binding energy were observed for the acid and base forms of the indicators on the Ti 6-4 surfaces. Different binding energies were detected for the oxygen photopeaks of bromthymol blue on Turco and phosphate-fluoride etched Ti 6-4 surfaces. More stearic acid was adsorbed from cyclohexane solutions on the Turco etched Ti 6-4 surface than on the phosphate-fluoride surface as detected by specular reflectance infra-red spectroscopy (SRIRS). A model for the Ti 6-4 surface was deduced based on the results above.

INTRODUCTION

Titanium 6-4 alloy is a highly stabilized alpha beta phase alloy with aluminum (6 wt %) as the alpha stabilizer and vanadium (4 wt %) as the beta stabilizer.[1] An important consideration for joining titanium alloys and indeed many metals by adhesive bonding is the surface pretreatment prior to bonding. A variety of specialized surface pretreatments for Ti 6-4 have been developed in the past decade ostensibly to improve the strength and durability of

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† Based on the M.S. thesis of Ranjani Siriwardane, Virginia Polytechnic Institute and State University, 1980.

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adhesive bonds. It has been suggested that acid-base interaction plays an important role in adhesive bonding.[2–5] In addition to adhesion, acid-base properties of solid surfaces may play a major role in corrosion and catalysis. Extensive work has been done in the past on acid-base properties of solids with high surface area. However, there are many instances where we deal with low surface area solids such as the substrates used in adhesion. Less work has been done in the past on the measurement of acid-base properties of these low surface area solids. The objective of this work was to investigate the acid-base properties of titanium 6-4 coupons (low surface area) after pretreatment by the Turco and phosphate-fluoride processes. For comparative purposes, a similar study was made on titania powders.

EXPERIMENTAL

The powders used in this study were precipitated titanium dioxide (TiO_2-I) obtained from Dr. G. D. Parfitt of Tioxide International and flame hydrolyzed titanium dioxide (TiO_2-II) obtained from Cabot Corporation and marketed as CAB-O-TI. Titanium 6-4 metal coupons were obtained from personnel at the NASA-Langley Research Center.

The powders were studied using the indicators benzeneazodiphenylamine (Eastman), methyl yellow (Aldrich), bromphenol blue (Thomas), *o*-nitrophenol (Fisher) and *p*-nitrophenol (Fisher). The indicators bromthymol blue (Chemical Dynamics), thymol blue (Pfatz), bromphenol blue (Thomas), bromcresol green (Fisher), and benzeneazodiphenylamine (Eastman) were used to study Ti 6-4 metal coupons. One mg of the indicators, which were used to study powders, were dissolved in 10 ml of toluene, methanol, cyclohexane, iso-octane, 100% ethanol and deionized water. The indicator solutions which were used to study Ti 6-4 metal coupons were prepared by dissolving 0.01 g of the indicators in 25 ml of deionized water. Benzeneazodiphenylamine was dissolved in iso-octane. Stearic acid (Fisher) was used in the adsorption studies.

Color changes of the indicators on equilibration with the powder surfaces were observed by adding 2 ml of the indicator solution to 1 mg of the powder. The maximum wavelengths of absorption (λ_{max}) of the acid and base forms of the indicator solutions were determined in separate experiments by absorption spectra obtained with a Hitachi 100-60 spectrophotometer.

The Turco 5578 and phosphate-fluoride pretreatments were carried out using the procedures described in the Appendix. Immediately after the pretreatment of the Ti 6-4 coupons, 0.3 ml of the freshly prepared indicator solutions were spread over an area of about 6 cm^2 and visual color changes were noted within 15 minutes. The coupons were allowed to dry for 4 hours and DRVS measurements were then made immediately using a Cary 14 spectrophotometer.

The effects of time, solvent and temperature on surface acidity were examined using thymol blue and bromthymol blue.

a) Time effects: After pretreatment, the metal samples were allowed to dry in quiescent air. The indicator solutions were spread on the metal samples after drying 1, 2, 10, 25, 50 and 100 hours and DRVS measurements were taken.

b) Solvent effect: Indicators were dissolved in ethanol and DRVS measurements were taken on the pretreated metal coupons as before.

c) Temperature effects: The pretreated metals were heated to 230°C for 10 hours in a Blue M forced air oven. Indicator solutions were spread after cooling and DRVS measurements were taken. Some of the metals were kept at room temperature for 90 hours and measurements were taken as before.

A Dupont 650 electron spectrometer with Mg K_α radiation (1254 eV) was used for the ESCA analysis of the bromthymol blue on the Ti 6-4 surface. Samples for the ESCA analysis were prepared by spreading 0.3 ml of the indicator solution on the pretreated metal samples. The samples were also immersed in the indicator solution for 4 hours. The indicator was also spread on metal surfaces on which a few drops of concd. hydrochloric acid had already been spread. Thus the acid form of the indicator was obtained directly on the surface. Narrow scan spectra were taken for the C 1s, O 1s, Br 3p, S 2p, Ti 2p and Na 1s photopeaks. Binding energies of the elements were corrected by taking the binding energy of C 1s photopeak due to surface contamination as 284.6 eV.[6] The precision in the measured binding energies is ±0.2 eV. Surface atomic fractions were calculated from measured areas of the respective photopeaks corrected using tabulated values[7] of the photoionization cross-sections. The error in the measured peak areas is estimated to be ±10%. Curve fitting of the unresolved O 1s photopeaks was done using GASCAP.

Adsorption of stearic acid from cyclohexane solutions was detected using a Pye Unicam SP240 specular reflectance unit attached to a Perkin Elmer 283 spectrometer. Samples were prepared by immersing the pretreated metal coupons in 0.001, 0.01 and 0.02 wt % stearic acid solutions for one hour.

RESULTS AND DISCUSSION

Study of solid powders

Titanium dioxide powders were chosen for study since the presence of an oxide layer on Ti 6-4 surfaces was shown in previous work.[8] Further, Walling[9] has previously reported similar measurements on TiO_2. The color changes of the adsorbed indicators are given in Table I. Powdered TiO_2-I was found to be very acidic and the surface acidity was <1.2. For the purpose of this paper, the definition of "surface acidity" is taken as the acidity comparable to an aqueous solution which has a pH value close to the pKa value of an indicator which is present in both acid and base forms in that solution. The term surface acidity defined in this way will be used henceforth. Thus, the surface acidity of TiO_2-I is <1.2, the pKa value of benzeneazodiphenylamine.

TiO_2-II powder was basic and the surface basicity was >7.2, the pKa value of *p*-nitrophenol. TiO_2-I is a titania powder obtained from Parfitt and has been shown to be rather hydrophilic. TiO_2-II is a flame hydrolyzed

TABLE I

Colour changes of the indicators on solid powders

Indicator	Solvent	TiO_2-I	TiO_2-II
Benzene azo diphenyl amine	Iso-Octane	Y → V	Y → Y
	Cyclohexane	Y → V	Y → Y
	Methanol	Y → Y	Y → Y
	Ethanol	Y → Y	Y → Y
	Toluene	Y → Y	Y → Y
Methyl yellow	Iso-Octane	Y → R	Y → Y
	Cyclohexane	Y → R	Y → Y
	Methanol	Y → R	Y → Y
	Ethanol	Y → Y	Y → Y
	Toluene	Y → R	Y → Y
Brom phenol blue	Methanol	B → Y	B → B
	Water	B → B	B → B
	Ethanol	B → Y	B → B
o-Nitro phenol	Iso-Octane	Y → C	Y → Y
	Cyclohexane	Y → C	Y → Y
	Ethanol	Y → C	Y → Y
	Toluene	Y → C	Y → Y
p-Nitro phenol	Water	Y → C	Y → Y
	Ethanol	C → C	C → Y
	Toluene	C → C	C → Y

B = Blue; C = Colorless; P = Pink; R = Red; V = Violet; Y = Yellow.

titania prepared from $TiCl_4$ and has been shown to be rather hydrophobic. These are quite significant results in that two TiO_2 powders having quite different surfaces can be differentiated readily by the indicator method. Walling[9] reported a pKa value of >3.3 for TiO_2.

Study of titanium 6-4 metal coupons with indicators

The Turco and phosphate-fluoride pretreatments are used in cleaning titanium 6-4 surfaces prior to adhesive bonding. Significant differences in surface morphology after these particular pretreatments have been observed previously by scanning electron microscopy.[10, 11] In the photomicrographs for the phosphate-fluoride etched Ti 6-4 sample, there appear fairly well defined grey and white areas corresponding to alpha and beta phases of the alloy, respectively. The beta phase crystals are poorly defined, but the alpha phase shows regularly-spaced edges approximately 100 nm apart. The Turco pretreated Ti 6-4 surface differs significantly from the phosphate/fluoride etched surface. The beta phase appears to have grown at the expense of the alpha phase and exists as highly fragmented structures. It is important to determine if these pretreated surfaces differ in surface acidity.

TABLE II

λ_{max} values and color changes of the indicators on pretreated Ti 6-4 surface

		Turco		Phosphate-Fluoride	
Indicator	pKa at zero ionic strength	Color change before drying	Color and λ_{max} (nm) value after drying	Color Change before drying	Color and λ_{max} (nm) value after drying
Benzeneazo diphenyl-amine	1.2	Y → Y	464 Y	Y → Y	436 Y
Bromphenol blue	4.1	B → B	635 B 436 (Weak)	B → B	636 (B) 436 (Weak)
Bromcresol green	4.9	G → B-G	644 B-G 460 (Weak)	G → B-G	610 (B-G) 472 (Weak)
Bromthymol blue	7.3	B → B	604 B	B → Y-B	464 Y
Thymol blue	9.2	B → Y	476 Y	B → Y	478 Y

B = Blue; G = Green; Y = Yellow; B-G = Blue-Green, Y-B = Yellow Blue.

Visual color changes and λ_{max} values from DRVS of the indicators on Ti 6-4 surfaces pretreated with the Turco and phosphate-fluoride processes are given in Table II. Only thymol blue changes color from the base form to the conjugate acid form on the Turco etched Ti 6-4 surface. The λ_{max} value is characteristic of the acid form. Thus the Turco etched surface is rather basic and its basicity lies between 7.3 and 9.2. Results from Table II also indicate that the Ti 6-4 surface after treatment with the phosphate-fluoride process is acidic and the acidity lies between 4.9 and 7.3.

Effect of experimental conditions

i) Time effects
ii) Effect of solvent
iii) Temperature effects

It is suspected that surface characteristics are modified when a freshly pretreated metal surface is exposed to the atmosphere. However, definitive experimental results supporting such changes are scarce. It is interesting to examine how the acid-base properties change when the surface is exposed to air. The color changes and λ_{max} values of bromthymol blue from DRVS are given in Table III for a phosphate-fluoride etched Ti 6-4 surface obtained

TABLE III

Time effects on phosphate-fluoride etched Ti 6-4 surface with bromthymol blue

Time (Hours)	Color change before drying	Color and λ_{max} (nm) value after drying
1	B → B-Y	444 Complete Y
2	B → B-Y	440 Complete Y
5	B → B-Y	448 Mainly Y with small B spots
10	B → B-Y	400; 630 Mainly Y with B spots
25	B → B-Y	456; 652 Mainly Y with B spots
50	B → B-Y	424; 648 Y with B spots
100	B → B-Y	444; 632 Y with B spots

B = Blue; B-Y = Blue-Yellow; Y = Yellow

at different time intervals after exposing to air. The blue base form of bromthymol blue appears after 10 hours. It is generally accepted in adhesion technology that if a freshly pretreated Ti 6-4 surface is not to be bonded within several hours, the surface should be primed for protection. Thus this work establishes the surface chemistry basis for the priming process, namely, to prevent changes in surface acidity leading to decreased bond strength. Time effects were not seen for the Turco etched surface.

In aqueous solutions, all the indicators existed in the base form. In ethanol solutions, the acid forms of bromcresol green and bromcresol purple were obtained. However, the results with ethanol solutions were consistent with what was observed with aqueous solutions.

When the pretreated metals were treated to 230°C for 10 hours, a drastic reduction of acidity was observed for the phosphate-fluoride etched surface and a slight reduction of basicity was observed for the Turco etched surface. However, these changes were not seen when the heated samples were kept at room temperature for another 90 hours.

Electron spectroscopy for chemical analysis (ESCA)

ESCA analysis was done to determine if shifts in binding energy were observed for the acid and base forms of the indicators. Previous work in our laboratory by Chen *et al.*[12] showed that trace amounts of fluorine, aluminum and vanadium are present on both the Turco and phosphate-fluoride etched Ti 6-4 surfaces and trace amounts of potassium, chlorine and phosphorous are present on the phosphate-fluoride etched surface.

The ESCA results for the Turco and phosphate-fluoride etched Ti 6-4 surfaces are listed in Table IV. Both freshly pretreated Ti 6-4 surfaces had a small Ti 2p3 photopeak at an average binding energy of 453.2 eV which was assigned to elemental titanium [Ti (O)] in addition to a large Ti 2p3 photopeak at 458.4 eV assigned to Ti (IV). The phosphate-fluoride etched surface had a larger Ti (O) signal relative to the Ti (IV) signal than the Turco etched surface. This shows the presence of a thicker oxide layer on the Turco etched surface consistent with the results reported by Ditchek *et al.*[13]

The oxygen 1s photopeak for the phosphate-fluoride etched surface was characterized by a narrow peak width at half-height [PWHH = 1.8 eV] and was centered at 530.1 eV as noted in Table IV. This single photopeak was assigned to lattice oxygen. However, the oxygen 1s photopeak for the Turco etched surface was asymmetric and significantly broader [PWHH = 2.8 eV] and therefore curve fitted into two component peaks as listed in Table IV. The major peak at a binding energy of 530.5 eV was again assigned to lattice oxygen. The second peak at 532.2 eV was attributed to adsorbed oxygen as suggested by Anderson.[14] An alternate assignment of the 532.2 eV photo-

TABLE IV

Results of the ESCA analysis of the Phosphate-fluoride (P-F) and Turco (T) etched Ti 6-4 surfaces and after spreading the Bromthymol Blue (BTB) on Phosphate-fluoride etched and Turco etched Ti 6-4 surfaces and Bromthymol Blue with HCl on the as-received (A-R) Ti 6-4 surface

	T		P-F		BTB/T		BTB/P-F		BTB + HCl/A-R	
Photopeak	B.E.(eV)	A.F.	B.E.(eV)	A.F.	B.E.(eV)	A.F.	B.E.(eV)	A.F.	B.E.(eV)	A.F.
C 1s	(284.6)	0.64	(284.6)	0.52	(284.6)	0.59	(284.6)	0.68	(284.6)	0.68
S 2p3		ND		ND	168.0	0.022	167.8	0.035	168.0	0.044
Br 3p3		ND		ND	183.7	0.014	183.5	0.015	183.6	0.037
Na 1s	1071.2	0.059		ND	1071.7	0.037	1071.7	0.049	1071.6	0.005
Ti(IV) 2p3	458.2	0.092	458.6	0.12	458.4	0.052	458.2	0.011	458.7	0.011
Ti(O) 2p3	453.0	0.002	453.4	0.004		ND		ND		ND
O 1s	530.5*	0.12	530.1	0.36	530.6*	0.16	530.8	0.07	530.7	0.08
	532.2	0.09		ND	532.4	0.09	532.4*	0.12	532.6*	0.10
					533.6	0.03	533.9	0.02	534.1	0.02

peak suggested by the reviewer is the presence of surface hydroxyl groups [i.e., $\geqslant$Ti—OH]. The ratio of the areas of the two peaks was 1.3.

The ESCA results obtained after spreading bromthymol blue on Turco and phosphate-fluoride pretreated Ti 6-4 coupons and also for bromthymol blue with HCl on the Ti 6-4 surface are given in Table IV. The presence of the bromthymol blue on the Ti 6-4 surface is indicated by the appearance of the S 2p3 and Br 3p3 photopeaks characteristic of the indicator.

The binding energies of the curve fitted O 1s photopeaks from the Ti 6-4 samples with the bromthymol blue are listed in Table IV. The predominant peak is noted by an asterisk. There are several points to note in Table IV. First, for bromthymol blue on either the phosphate-fluoride etched surface or the bromthymol blue + HCl on the Ti 6-4 surface, the major peak is now at 532.5 eV. This peak, which was not present on the original phosphate-fluoride etched surface, is assigned to oxygen from the bromthymol blue indicator in the *acid* form on the surface.

Secondly, for bromthymol blue on the Turco etched surface, the peak at 530.5 eV is assigned to both lattice oxygen and to oxygen from the bromthymol blue in the *base* form on the surface. This conclusion is based on the significant increase in the ratio of the areas of the 530.5 eV to the 532.3 eV photopeaks when comparing the bromthymol blue on the Turco etched surface to the original Turco etched surface. There is thus a shift of 2.0 eV in the O 1s photopeak between the acid and base form of the bromthymol blue. From DRVS studies it was seen that the acid form of the bromthymol blue was present on the phosphate-fluoride etched surface while the base form was present on the Turco etched surface. The structures are different for the acid and base forms. The oxygen is negatively charged in the base form while it is protonated in the acid form. Thus the oxygen being more negative in the base form is expected to have a lower binding energy than the acid form. Thus the results obtained from the ESCA analysis are consistent with the results expected from the structural formulas. The above results indicate that the acid and base forms of the indicators having different structures can be monitored using ESCA technique.

Finally, a third O 1s photopeak having an average binding energy of 533.9 eV was necessary to obtain a proper curve fit to the composite oxygen 1s photopeak. This small peak was unassigned but presumably due to some oxygen moiety in the bromthymol blue molecule since it only appeared when the indicator was present on the Ti 6-4 surface.

When the pretreated metals were simply immersed in the bromthymol blue solution, photopeaks characteristic of sulfur and bromine were observed.[15] This indicates that there is adsorption of the indicator onto the metal coupons. However the S/Ti atomic fraction ratio was 0.06 and 0.12 for the Turco and phosphate fluoride etched surfaces, respectively. The larger ratio for the phosphate-fluoride etched surface indicates greater adsorption of bromthymol blue which was present in its base form onto this acid etched surface.

Specular reflectance infra-red spectra (SRIRS)

Differences in surface acidity of Ti 6-4 should lead to differences in the amount of stearic acid adsorbed from cyclohexane solutions. A basic surface would be expected to adsorb more stearic acid than an acidic surface. Peak intensities from SRIRS after immersing the etched surfaces in a 0.001 %, 0.01 % and 0.02 % by weight stearic acid solutions were measured. The intensities were higher on the Turco etched surface indicating that there is more adsorption of stearic acid onto the Turco etched surface than onto the phosphate-fluoride etched surface. This difference is illustrated in the

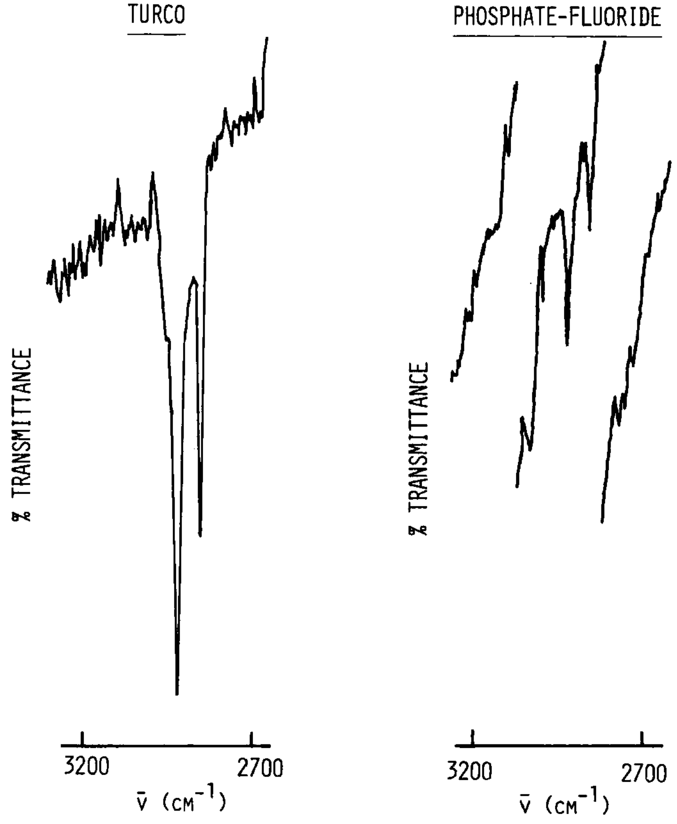


FIGURE 1 Specular reflectance infrared peaks in the region 2700–3200 cm^{-1} of stearic acid adsorbed on Ti 6-4 surfaces.

intensities of 2920 cm^{-1} peaks for the 0.02% concentration as shown in Figure 1. The infra-red results are consistent with the results obtained by indicator method. That is, the more basic Turco etched Ti 6-4 surface adsorbed more stearic acid than the more acidic phosphate-fluoride etched surface. SRIRS can be used in the study of surface acidity. However the results of SRIRS give only a relative measure of surface acidity whereas the indicator method gives a quantitative measure.

A model for the Ti 6-4 surface

A model for the Ti 6-4 surface can be deduced to account for the surface acidity based on the results described above. It is important to note that both Lewis and Bronsted sites can interact with the indicators to change the color. The phosphate-fluoride pretreatment involved the reaction with HF(aq) and indeed F 1s photopeaks were observed with ESCA.[12] The Bronsted acidity may be due to the functional groups shown in Figure 2.

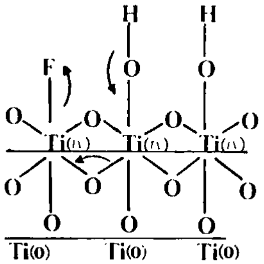
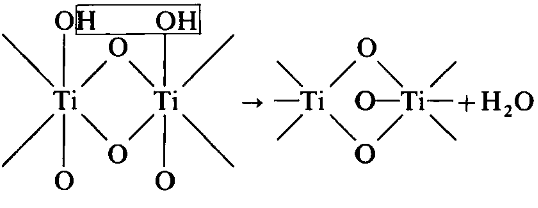


FIGURE 2 Acid sites on Ti 6-4 surface after phosphate-fluoride pretreatment.

The acidity of the —OH groups may be due to the weakening of the —OH bond by the inductive effect of the highly electronegative fluorine.[16] When the phosphate-fluoride etched surface was exposed to air, the decrease in acidity after 10 hours may be due to oxidation of Lewis sites or adsorption of basic impurities like NH_3 from laboratory environment. When the treated metal was heated to 230°C, the acidity decreased drastically. Removal of water and condensation of adjacent hydroxyl groups as shown in reaction [1] can take place at higher temperature removing Bronsted acid sites.



[1]

Since this decrease in acidity was not observed when the heated metal was placed at room temperature for 90 hours, this reaction has to be reversible over 90 hour period.

In contrast to phosphate-fluoride etched surface, the Turco etched surface was basic. The $—O^{\ominus}$ centers formed by reaction [2] may be the basic sites on Turco etched surface.

$$—M—OH+OH^{\ominus} \rightarrow —M(OH)_2^{\ominus} \rightleftarrows —MO^{\ominus}+H_2O \qquad [2]$$

CONCLUSIONS

The TiO_2 powders having different surfaces can be readily differentiated by the indicator method. The solid powder TiO_2-I was found to be acidic and the surface acidity <1.2. The TiO_2-II powder was basic and the surface basicity >7.2.

The indicator method and DRVS measurements can be used to differentiate the acid-base characteristics of Ti 6-4 surfaces after different pretreatments. The Turco etched Ti 6-4 surface was basic and the basicity lies between 7.3 and 9.2. The phosphate-fluoride etched Ti 6-4 surface was acidic and the acidity lies between 5.4 and 7.3. A decrease in surface acidity was found with bromthymol blue when the phosphate-fluoride etched Ti 6-4 surface was exposed to air for 10 hours. Surface acidities established using aqueous solutions of the indicators and ethanol solutions of the indicators were in good agreement. When the pretreated Ti 6-4 metals were heated to 230°C, a decrease in basicity was observed on the Turco etched Ti 6-4 surface and a drastic decrease in acidity was observed on phosphate-fluoride etched Ti 6-4, using bromthymol blue.

Binding energies of oxygen for bromthymol blue on Turco and phosphate-fluoride etched Ti 6-4 surfaces were different as detected by the ESCA technique. Thus the acid and base forms of the indicators having different structures can be monitored by ESCA technique.

More stearic acid was adsorbed on the Turco etched Ti 6-4 surface than on the phosphate-fluoride etched Ti 6-4 surface as detected by SRIRS. This result is consistent with the greater basicity of the Turco etched Ti 6-4 as determined by the indicator method.

Acknowledgements

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APPENDIX

A detailed description of the two surface pretreatments is given below.

Phosphate/Fluoride Treatment

1. Solvent wipe—methylethyl ketone.
2. Alkaline clean—immerse in SPREX AN-9, 30.1 g/l, 80°C for 15 min.
3. Rinse—deionized water at room temperature.
4. Pickle—immerse for 2 min. at room temperature in solution containing 300 g/l of 70% nitric acid and 31 g/l of 48% hydrofluoric acid.
5. Rinse—deionized water at room temperature.
6. Phosphate/fluoride treatment—Soak for 2 min. at room temperature in solution containing 50.3 g/l of tri sodium phosphate; 20.5 g/l of potassium fluoride; and 29.1 g/l of 48% hydrofluoric acid.
7. Rinse—deionized water at room temperature.
8. Hot water soak—deionized water at 65°C for 15 min.
9. Final rinse—deionized water at room temperature.
10. Dry—air at room temperature.

Turco 5578 Treatment

1. Solvent wipe—methylethyl ketone
2. Alkaline clean—immerse in Turco 5578, 37.6 g/l, 70–80°C for 5 min.

3. Rinse—deionized water at room temperature.
4. Etch—immerse in Turco 5578, 419 g/l, 80–100°C for 10 min.
5. Rinse—deionized water at room temperature.
6. Rinse—deionized at 60–70°C for 2 min.
7. Dry—air at room temperature.