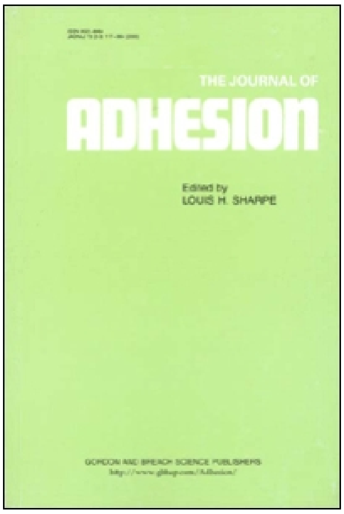

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Siriwardane, Ranjani V. and Wightman, J. P.(1983) 'Surface Characterization of Ti and Ti (6% AI-4%, V) Metal Powders and Interaction with Primer Solutions', The Journal of Adhesion, 15: 3, 225 — 239
To link to this Article: DOI: 10.1080/00218468308073229
URL: http://dx.doi.org/10.1080/00218468308073229

J. Adhesion, 1983, Vol. 15, pp. 225–239
0021-8464/83/1504-0225 $18.50/0

Printed in Great Britain

Surface Characterization of Ti and Ti (6%, Al–4%, V) Metal Powders and Interaction with Primer Solutions†

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(*Received July 12, 1982; in final form November 16*, 1982)

The surfaces of Ti and Ti (6% Al–4% V) powders were characterized by several techniques. BET surface areas as a function of temperature were measured using nitrogen adsorption. Heats of immersion ($\Delta_w H$) of these metal powders in water were measured after evacuation over the temperature range 100°–400°C. The $\Delta_w H$ in water increased with increasing evacuation temperature and an anomalous increase was observed between 300° and 400°C. This was attributed to exposure of water to elemental titanium by cracking of the oxide layer at 400°C. XPS analysis did not support the possibility of metal migration through the oxide layer. Higher heats of immersion in water were determined for chemically pretreated compared to untreated Ti 6–4 powders. Water vapor adsorption isotherms were measured after evacuation of the metal powders at 100°C. Partial irreversibility of the water adsorption was observed on both powders. Water adsorption on Ti was temperature dependent. Heats of immersion measurements were used to study the interaction of primer solutions with these metal powders. Polyimide (LARC-13) and polyphenylquinoxaline (PPQ) interacted preferentially compared to the solvents with both powders. This polymer-metal interaction improved significantly after pretreatment of the Ti 6–4 powder by the Turco® 5578 and phosphate-fluoride processes. Again, an anomalous increase in the heat of immersion of Ti 6–4 evacuated at 400°C in the primer solution/solvents was observed. Anatase and rutile TiO_2 powders are not satisfactory models for the surface oxide layer on either Ti or Ti 6–4 powders.

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† Based in part on the Ph.D. Dissertation of R.V.S., Virginia Polytechnic Institute and State University, 1981.

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INTRODUCTION

Adhesives are being used increasingly to bond metal structural components. For example, an extensive effort is underway to adhesively bond Ti (6% Al–4% V) in advanced aircraft.[1] The strength and durability of these adhesive bonds depend in part on the properties of the oxide layer present on the alloy surface. A number of experimental techniques including electron spectroscopy for chemical analysis,[2,3] scanning (transmission) electron microscopy,[3] reflectance visible-infrared spectroscopy,[4] secondary ion mass spectrometry,[5] Auger electron spectroscopy[6,7] and ion scattering spectroscopy[6,7] have been used to characterize this oxide layer. It has been reported[8] that the layer on the Ti 6–4 surface may indeed be the rutile phase of TiO_2. Shih *et al.*,[9] however, found that the final structure of the oxide was probably TiO not TiO_2. Several chemical pretreatments have been developed to clean the alloy surface to obtain better adhesive bonding.[7] The effect of these chemical pretreatments on properties of the oxide layer is of considerable interest as well as the interaction between adhesives and the oxide layer. However, it is difficult to study the interaction of polymeric adhesives with the oxide layer on minimal surface area Ti 6–4 metal coupons such as are used in lap shear testing. To overcome this difficulty, Ti metal and Ti 6–4 metal in the form of powders were used in this study of their interaction with water and primer solutions. Similar comparative studies have been made in our laboratory on pure crystalline titanium dioxide powders.[10]

EXPERIMENTAL

Titanium and titanium 6–4 powders were obtained from Cerac Corp. Surface areas of the powders were determined by the BET method as described by Gregg and Sing,[11] using a Micrometrics 2100D surface area analyzer. Prior to the surface area measurements, the powders were evacuated for 1 hour over the temperature range 100°–400°C at 10^{-5} torr. SEM photomicrographs were taken using an Advanced Metals Research Corporation 900 scanning electron microscope operating at 10 KV. EDAX® spectra were performed using an International 707A unit attached to the microscope. XPS analysis was done on untreated metal samples and samples heated in vacuo (10^{-7} torr) at 400°C using a duPont 650 photoelectron spectrometer with a Mg K_α (1253.6 eV) source.

Water vapor adsorption measurements were done manometrically in a constant volume system constructed with Teflon® stopcocks. Samples were heated for 2 hours under vacuum at the evacuation temperature. The quantity of water adsorbed was calculated assuming ideal gas behavior. Readsorption isotherms were determined after heating equilibrated samples at the specified temperature for 2 hours.

Heats of immersion of the powders in water and in primer solutions were determined in a Calvet MS 70 microcalorimeter. The samples were evacuated in glass ampoules with break-off tips at 10^{-5} torr for 2 hours at different temperatures and sealed under vacuum. The polymers polyphenylquinoxaline (PPQ) and polyimide (LARC-13) were obtained from personnel at the NASA–Langley Research Center. Preparation of these polymers has previously been reported.[12,13] A 5 wt % PPQ primer solution was prepared by dissolving the polymer in a 1 : 1 mixture of xylene and m-cresol. Dimethyl formamide was used in the preparation of a 22 wt % LARC-13 solution. Heats of immersion of the powders in the two solvents and in the primer solutions were determined after evacuation of the powders at room temperature for 24 hours at 10^{-5} torr. The Ti 6–4 powders were pretreated an alkaline etch [Turco® 5578] and an acidic phosphate–fluoride etch as described previously.[4]

RESULTS AND DISCUSSION

Characterization of Ti and Ti 6–4 metal powders

The SEM photomicrographs of untreated Ti and Ti 6–4 surfaces are shown in Figure 1. The surface of Ti appears smooth compared to the surface of Ti 6–4 which consists of more secondary particles. EDAX analysis showed only Ti present in both powders. It is interesting to note that vanadium and aluminum were not detected on untreated Ti 6–4 particles. However, the EDAX analysis did show aluminum on Ti 6–4 after evacuation at 400°C. The surface areas of Ti and Ti 6–4 metal powders determined at different evacuation temperatures (T_{0G}) are shown in Table I. A significant increase in the surface area of both powders was found for evacuation temperatures between 300° and 400°C.

Interaction of water with Ti and Ti 6–4 metal powders

It is essential to understand the role of water in adhesion involving oxide

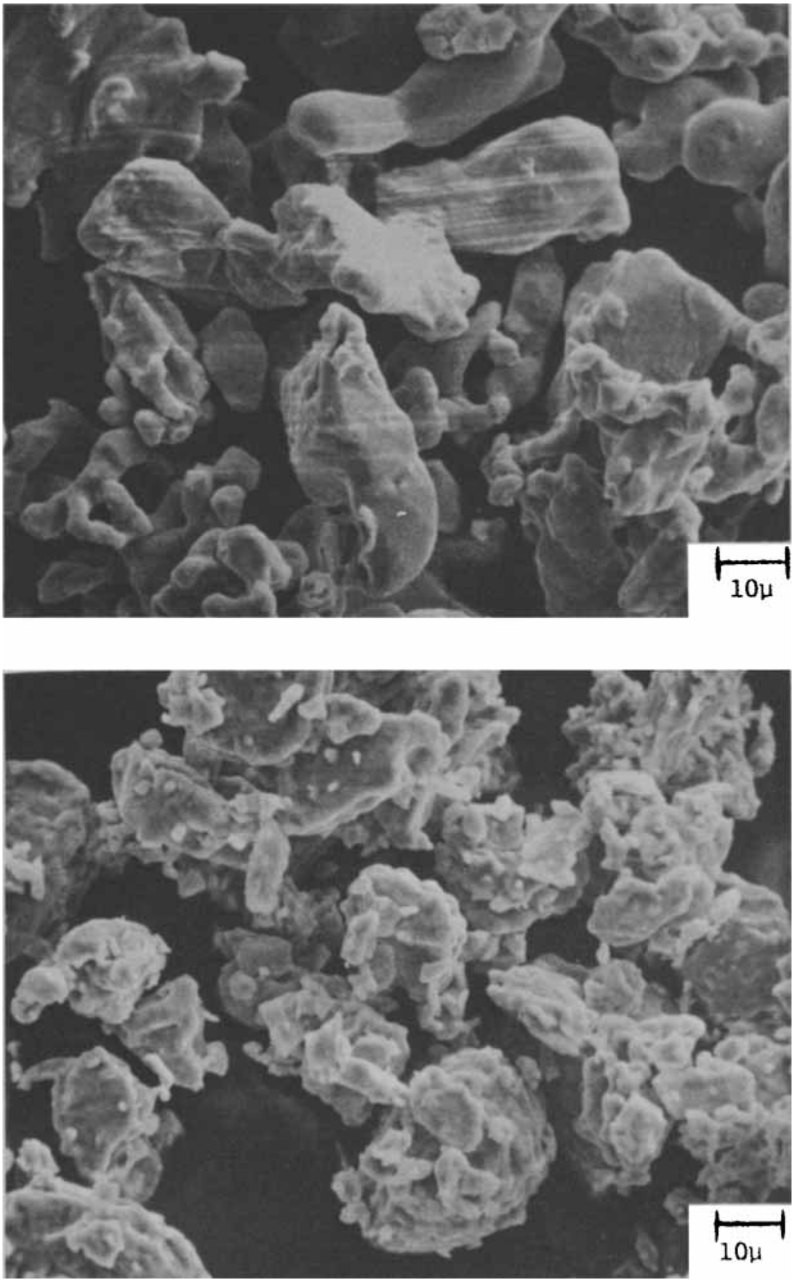

FIGURE 1 Scanning electron photomicrographs of (a) Ti and (b) Ti 6–4 powders.

TABLE I
Surface areas of Ti and Ti 6–4 powders

Powder	T_{0G}(°C)	Surface Area (m^2/g)
Ti	100	0.25
	200	0.26
	300	0.28
	400	0.45
Ti 6–4	100	0.13
	200	0.12
	300	0.17
	400	0.22

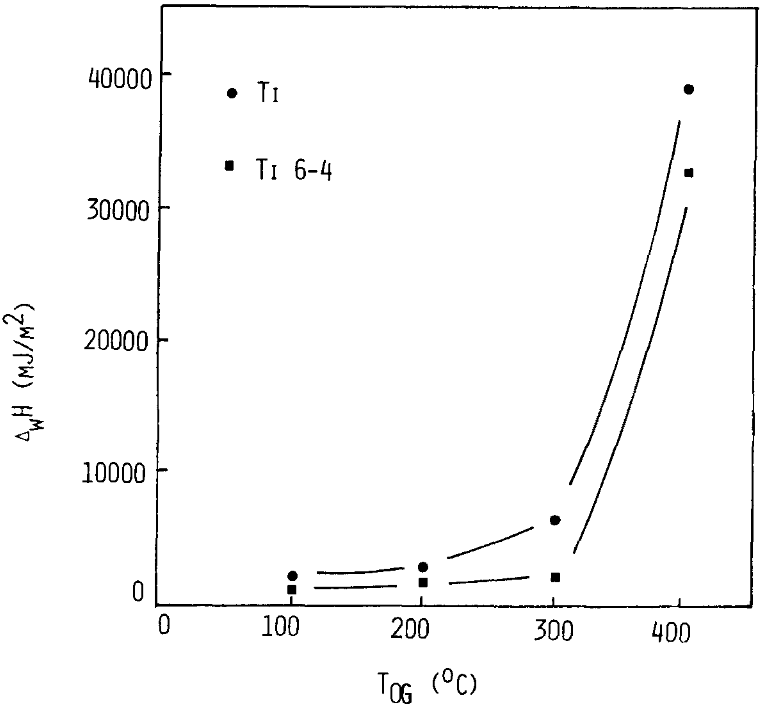

FIGURE 2 Heats of immersion of Ti and Ti 6–4 powders in water as a function of evacuation temperature.

surfaces. Heats of immersion of metal powders in water as a function of evacuation temperature are shown in Figure 2. The heats of immersion per unit area are higher (see Table IV) than what was observed with crystalline titanium dioxide powders recently reported.[10] The heats

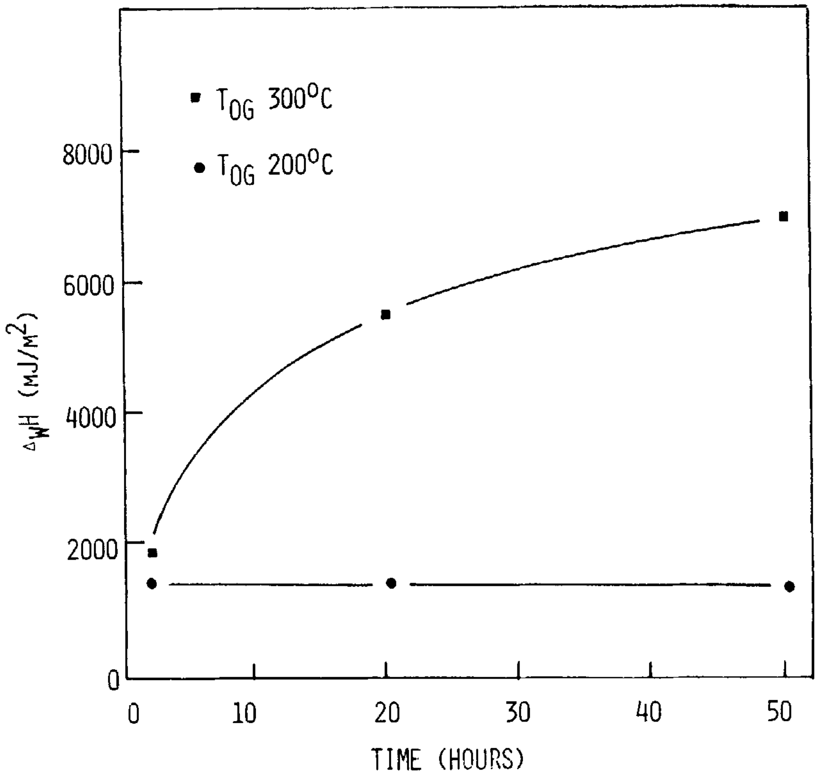

FIGURE 3 Heats of immersion of Ti 6–4 in water as a function of evacuation time at 200° and 300°C.

of immersion increased with increasing evacuation temperature. A dramatic increase in heats of immersion on evacuation between 300° and 400°C was observed for both powders. This increase in heat is not due to an increase in surface area since the heats of immersion have been normalized on a unit area basis. Further, the time required for the calorimeter to return to steady state was significantly longer for the 400°C than for the 100°C evacuation case. To investigate further this increased heat of immersion, the Ti 6–4 powder was evacuated for 20 hours and 50 hours at 200°C and 300°C, and heats of immersion were measured. As shown in Figure 3, there was no change in the heat of immersion in water of Ti 6–4 with evacuation time at 200°C. However, there was an increase in $\Delta_w H$ with increasing evacuation time at 300°C. Thus the increase in heats of immersion observed between 300° and

TABLE II
XPS analysis of Ti and Ti 6–4 powders

Element	Ti		Ti T_{OG} 400°C		Ti 6–4		Ti 6–4 T_{OG} 400°C	
	B.E. (eV)	A.F.	B.E. (eV)	A.F.	B.E. (eV)	A.F.	B.E. (eV)	A.F.
C 1s	(284.6)	0.43	(284.6)	0.18	(284.6)	0.50	(284.6)	0.32
Al 2s	118.6	0.018	118.9	0.03	118.2	0.029	118.7	0.032
N 1s	—	—	—	—	399.3	0.010	398.7	0.02
Na 1s	1070.5	0.006	1071.7	0.02	—	—	—	—
O 1s	529.3	0.43	529.9	0.64	529.6	0.36	530.0	0.48
Ti (IV) 2p3	457.9	0.12	458.0	0.12	458.0	0.079	458.4	0.11
Ti (O) 2p3	453.6	0.001	453.6	0.004	453.4	0.001	454.1	0.003
V 2p3	—	—	—	—	516.0	0.005	521.2	0.03

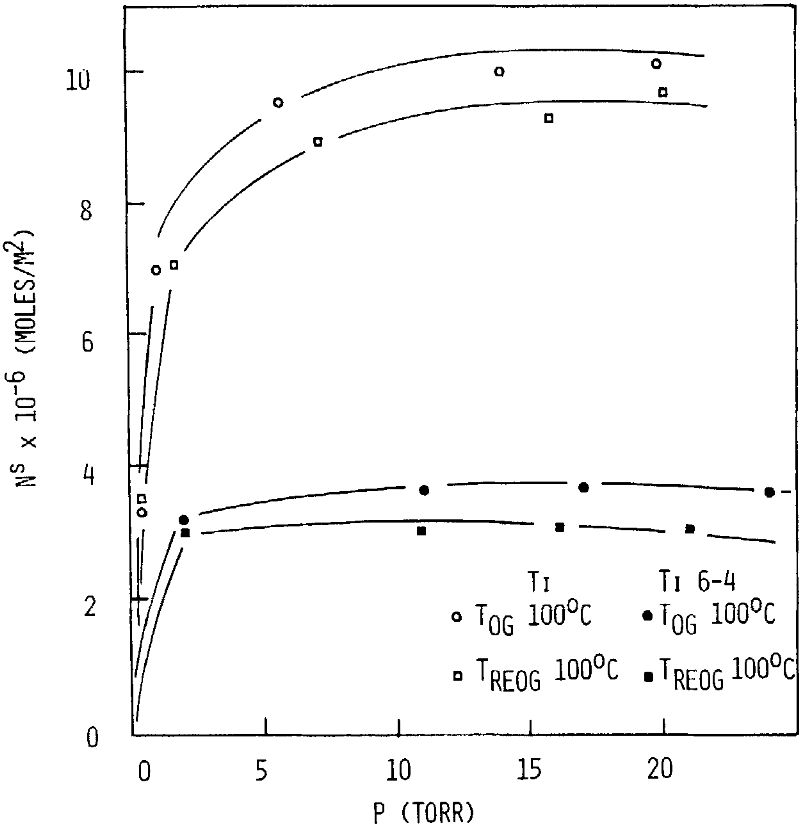

FIGURE 4 Adsorption and readsorption isotherms at 30°C for water on Ti and Ti 6–4 evacuated at 100°C.

400°C is a time dependent process. The long equilibration time and large heat of immersion after evacuation at 400°C indicates a strong chemical reaction. This is most likely due to the exposure of elemental Ti(0) at 400°C and its subsequent reaction with water.

Elemental Ti could be exposed on an oxide surface in different ways at elevated temperatures. Metal could migrate through the oxide layer by a cation diffusion mechanism. However, this cation diffusion on Ti metal has been observed previously only at 1000°C.[8]

To further investigate cation diffusion as a possible mechanism of metal exposure, XPS analysis was carried out on the metal powders at room temperature and after evacuation at 400°C in situ in the XPS spectrometer. The results of this XPS analysis are shown in Table II.

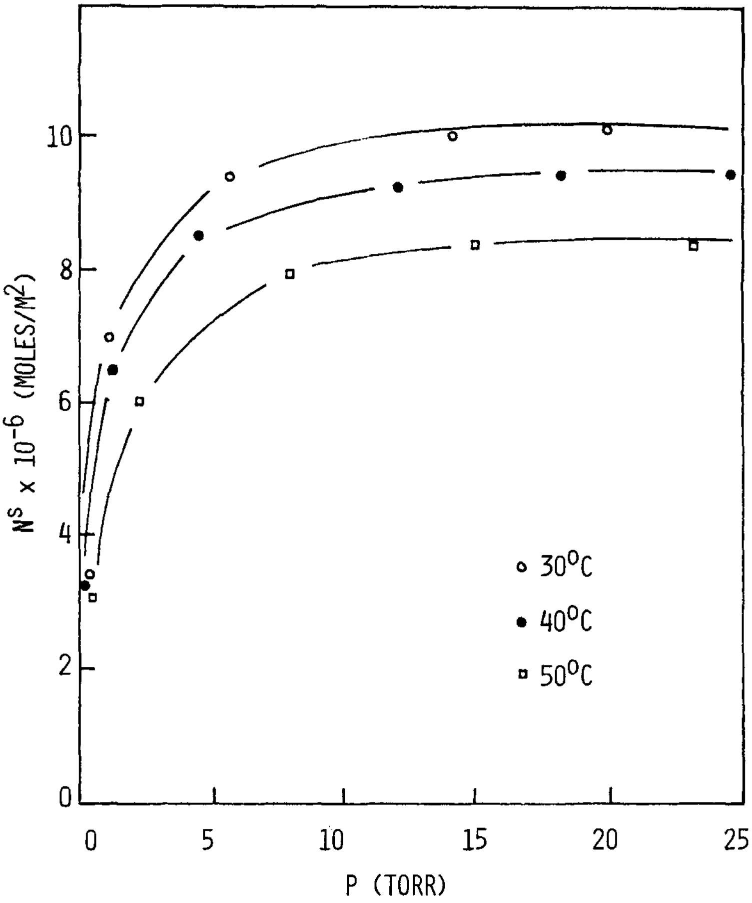

FIGURE 5 Temperature dependence on water adsorption isotherms of Ti evacuated at 100°C.

Binding energies (B.E.) of each photopeak are noted and the calculated atomic fractions (A.F.) of each element are listed. A small elemental titanium photopeak was observed on both Ti and Ti 6–4 surfaces at room temperature. Trace amounts of Na and Al were observed on the Ti 6–4 surface. After evacuation at 400°C, there was no significant increase in the amount of elemental titanium on the Ti 6–4 surface. Thus, the mechanism for the exposure of elemental titanium at 400°C is probably not cation diffusion.

A second mechanism of metal exposure is the cracking of the oxide layer at temperatures >200°C. Here, water can penetrate through the

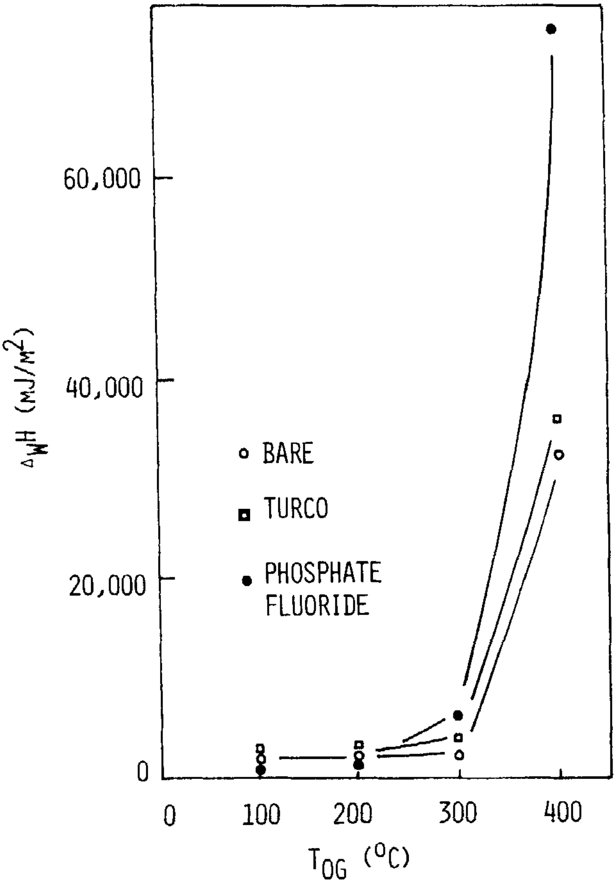

FIGURE 6 Heats of immersion of Ti 6–4 in water after Turco and phosphate-fluoride pretreatments as a function of evacuation temperatures.

cracks to react with the metal. Recent STEM work by Venables[14] and co-workers on Ti 6–4 shows that the amorphous oxide layer converts to a crystalline oxide at temperature >300°C. Such a conversion could be accompanied by volume changes leading to cracking of the oxide layer. Wefers[15] has shown that a similar phenomenon occurs with aluminum; that is, an enhanced uptake of oxygen is observed for aluminum heated to 600°C due to exposure of Al(0) on cracking of the oxide layer. The effect of evacuation temperature on the surface oxide of Ti 6–4 has profound implications on thermal aging studies of adhesive samples.

Water vapor adsorption and readsorption isotherms at 30°C for Ti and Ti 6–4 after evacuation at 100°C are shown in Figure 4. The readsorption isotherm was lower than the adsorption isotherm for both Ti and Ti 6–4 powders. This indicated that there was some irreversible adsorption of water vapor on Ti and Ti 6–4 powders after evacuation at 100°C. Furthermore, a lower water adsorption capacity per unit area was observed for Ti 6–4 compared to Ti. The adsorption of water vapor on Ti evacuated at 100°C varied inversely with temperature as shown in Figure 5.

Surface properties of Ti 6–4 powders after Turco and phosphate-fluoride pretreatments were further investigated since significant improvements in adhesive bonding have been observed following these pretreatments.[16] The surface areas of Ti 6–4 pretreated with Turco and phosphate-fluoride processes and evacuated at 100°C were 0.25 m^2/g and 0.24 m^2/g respectively. There is an appreciable increase in surface area after both the pretreatments. There were no significant differences in powder morphology after either pretreatment. EDAX analysis showed the presence of aluminum on the phosphate-fluoride etched surface. The heats of immersion in water of Ti 6–4 after the phosphate-fluoride and Turco pretreatments are shown in Figure 6. The heats of immersion of the untreated and pretreated powders were similar up to a 200°C evacuation temperature. However, at 200°C the heats of immersion were slightly higher on the pretreated surface than on the untreated surface. At 400°C the phosphate-fluoride etched surface showed a significantly higher heat of immersion compared to both Turco etched and untreated Ti 6–4 surfaces. It has been shown by previous workers[17] that Ti 6–4 samples pretreated with the phosphate-fluoride process results in only a thin oxide layer. Therefore exposure of elemental titanium by cracking of this thinner oxide layer could be easier.

Interaction of primer solutions with Ti and Ti 6–4 metal powders

Heats of immersion of the metal powders in primer solutions were used to study the interaction of the titanium surfaces with the polymeric adhesives. The importance of proper wetting of the adhesives on adherend surfaces has previously been recognized by various workers.[18,19] Molecular forces of attraction cause the adhesive to wet and spread on the surface.[19] Contact angles have been used widely to assess the wetting of solid surfaces by liquids.[20] Heats of immersion are another measure of the adhesion or interfacial forces between the liquid and the solid surface. In this study, the heats of immersion of the metal powders were measured in primer solutions and compared to those measured in the solvents. Any increase in the heat of immersion in the primer solution compared to that in the solvent was used as a measure of the interaction between the polymer and the metal. This procedure has been used previously by Zettlemoyer *et al.*[21] to study the adsorption of surfactants from aqueous solutions onto Graphon.

Heats of immersion of Ti and Ti 6–4 evacuated at room temperature, before and after Turco and phosphate-fluoride pretreatments, in LARC-13 solution, DMF, PPQ solution, and xylene + m-cresol are shown in Table III. The heats of immersion in LARC-13 solutions were significantly higher than those in DMF for both the Ti and Ti 6–4 powders. Thus LARC-13 interacts preferentially with Ti and Ti 6–4 metal powders in contrast to the results[10] for crystalline titanium dioxide powders.

TABLE III
Heats of immersion (mJ/m^2) of Ti and Ti 6–4 powders before pretreatment and of Ti 6–4 powder after pretreatment

Sample	DMF	LARC-13/DMF	Xylene : m-Cresol	PPQ/Xylene : m-Cresol
1. Ti	1065 ± 1.53	1492 ± 60	891 ± 54	1262 ± 147
2. Ti 6–4	233 ± 70	745 ± 36	284 ± 90	693 ± 4
3. Ti 6–4/Turco	1077 ± 100	2484 ± 150	924 ± 60	2319 ± 200
4. Ti 6–4/ Phosphate-Fluoride	1445 ± 150	3298 ± 200	1276 ± 150	2073 ± 250

The heats of immersion for the two metal powders in PPQ solutions were significantly higher than the heats of immersion in xylene + m-cresol. This indicates again that PPQ also preferentially interacts with metal powders. Both PPQ and LARC-13 are used to bond Ti 6–4 in structures.[1] Since molecular attractive forces contribute to the heats of immersion, the above observations serve to re-emphasize that molecular forces play an important role in metal–polymer bonding.

It is also interesting to note that the difference in heats of immersion between the polymer solutions and solvents increased considerably after pretreatment of the Ti 6–4 as shown by the results in Table III. Thus, here is calorimetric evidence that pretreatment processes can enhance the interaction between the polymer and Ti 6–4 surface and further

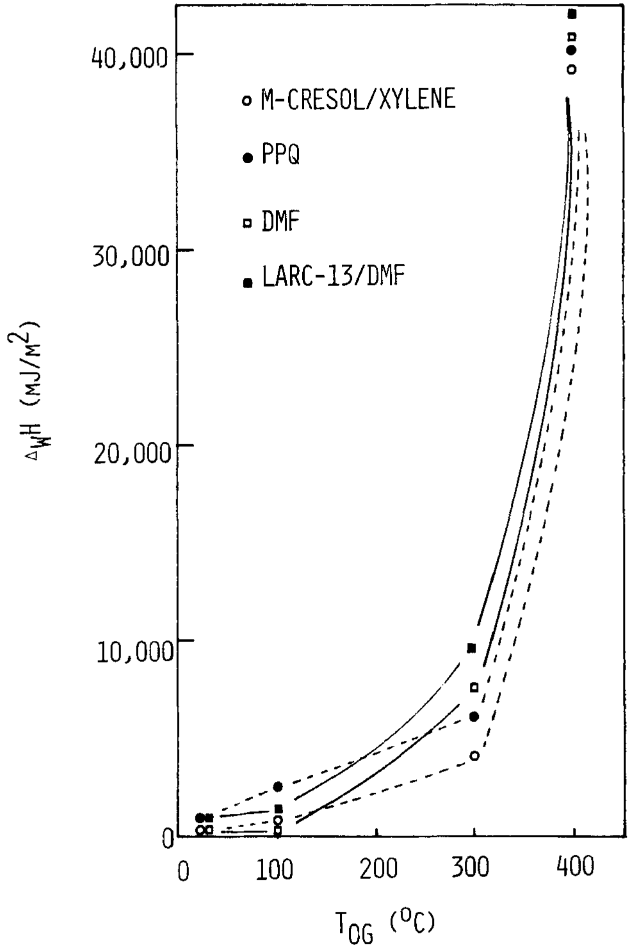

FIGURE 7 Heats of Immersion of Ti 6–4 in Polymer Solutions as a Function of Evacuation Temperature.

confirms the importance of surface pretreatment in metal–polymer bonding.

Heats of immersion of Ti 6–4 in the two primer solutions and in the respective solvents as a function of evacuation temperature are shown in Figure 7. The larger heat of immersion for both primer solutions compared to the solvent persists at each evacuation temperature. Further, the anomalous increase in the heat of immersion for Ti 6–4 evacuated at 400°C is seen here as was the case for water. Again, the

TABLE IV
Comparison of the properties of crystalline titanium dioxide powders with Ti and Ti 6–4 metal powders

Property	TiO_2	Ti and Ti 6–4
1. Heats of Immersion in water		
(a) T_{0G} 100°–300°C	400–800 mJ/m^2	1000–6000 mJ/m^2
(b) T_{0G} 400°C	400–1000 mJ/m^2	32000–39000 mJ/m^2
2. Water Vapor Adsorption	Fully reversible	Partially reversible
3. Surface Area	10–20 m^2/g	0.1–0.2 m^2/g
4. Interaction with LARC-13 solution	No preferential interaction	Preferential interaction
5. Interaction with PPQ PPQ solution	Only anatase shows preferential interaction	Preferential interaction

chemical reaction of polar liquids with elemental titanium results in the high heats of immersion.

There are marked differences between the properties of pure crystalline titanium dioxide powders observed in previous work[10,22] and the oxide surfaces present on the metal powders as shown in Table IV. For instance, water adsorption was completely reversible on crystalline powders while it was partially reversible on metal powders. Both primer solutions interacted preferentially over the solvents on the metal powders while only anatase titanium dioxide showed preferential interaction with PPQ. Finally the anomalous increase in the heat of immersion in water and in primer solutions on evacuation of both metal powders between 300° and 400°C was not observed for crystalline titanium dioxide powders. Clearly, crystalline titanium dioxide powders are not a good choice to simulate the oxide surfaces present on either Ti or Ti 6–4 coupons.

CONCLUSIONS

The surface oxide layer of Ti and Ti 6–4 cracked on heating in vacuo between 300° and 400°C as evidenced by quite high heats of immersion in both water and primer solutions. The polymers LARC-13 and PPQ interacted preferentially compared to the solvents with both metal powders after outgassing at room temperature. Heats of immersion of Ti 6–4 in water, solvents and primer solutions were increased significantly for Ti 6–4 pretreated by Turco and phosphate–fluoride processes compared to the untreated powder. The titanium dioxide powder surface is not a good model for the surface oxide layer on either Ti or Ti 6–4 powder.

Acknowledgements

Appreciation is extended to Mr. Andy Mollick and other members of the University Glass Shop for their great help in providing the necessary custom made glassware for the adsorption studies and for the calorimetry work. We thank Dr. Lucian Zelazny for the use of the surface area analyzer and Mr. Bob Honeycutt for obtaining the SEM photomicrographs. The technical assistance of Paul Hergenrother, Don Progar and Terry St. Clair at the NASA-Langley Research Center is recognized. Partial financial support for this research under NASA Grants NSG-1124 and NAG-1-124 is acknowledged.

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