

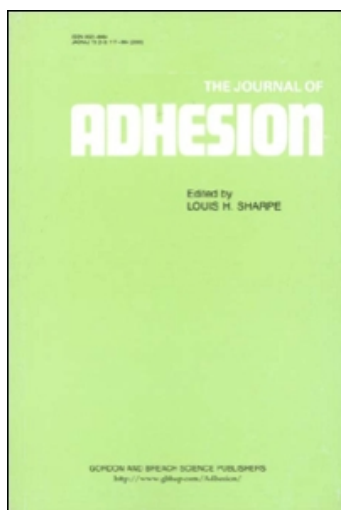
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Titanium and Alloy Surfaces for Adhesive Bonding

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The nature of the oxide on the surface of titanium and the Ti-6Al-4 V alloy after a number of recommended treatments has been examined by x-ray and electron diffraction. No evidence for material other than titania in its rutile form was obtained even though anatase and fluoride have been reported. The most efficient surface for adhesive bonding is a rough surface of the black oxide such as is produced by treatment of the metal in alkaline hydrogen peroxide.

INTRODUCTION

It is necessary and common practice to give a chemical treatment to titanium alloys before adhesive bonding or cold welding. A number of different treatments are advocated and reports of their efficacy vary. In an effort to simplify the problems "pure" titanium has sometimes been studied and the results extrapolated to the industrially important alloys. However, the impurities present in commercial titanium vary, depending upon the source and method of preparation and conflicting reports on the nature of the treated surface and on the preferred treatment may well be attributable to the different impurities in the samples used.

For example, with pure titanium Chiganova and Batashev¹ report in convincing detail the formation of layers of non-stoichiometric titanium hydrides, when sulphuric or hydrochloric acid is used for treatment. Under similar conditions Koizumi and Nakayama² report the presence of anatase and brookite in addition to the rutile form of titanium dioxide.

Similar differences occur with titanium alloys. For the important Ti-6Al-4 V alloy, with a phosphate-fluoride treatment, Hamilton³ found anatase changing very slowly (5-10 months) to the more stable rutile, and Capriolo

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and Turris⁴ reported only a fluoride, although they do not disclose how this was established.

MATERIALS

The Ti-6Al-4V was supplied by Imperial Metal Industries Ltd., (IMI 318) who give the composition as:

Aluminium, 5.5–6.75%; Vanadium, 3.5–4.5%; Iron, 0.30% maximum; Hydrogen, 0.12%; Titanium, 90.6–88.3%.

The commercially pure titanium was supplied by B.D.H. Chemicals Ltd. (Code IMI 115) of typical composition:

Aluminium, 0.05%; Vanadium, 0.05%; Iron, 0.025%; Hydrogen, 0.002–0.004%; Oxygen, 0.07%; Carbon, 0.02%; Titanium, 99.7%.

In both alloy and commercially pure titanium traces of other metal will occur.

EXPERIMENTAL

Discs 4 mm in diameter were punched from the original metals and were initially electropolished in 5% w/v perchloric acid in glacial acetic acid with a current density of 0.5 amp/cm². They were then subjected to various chemical etch treatments as detailed below.

Topographical features were studied by carbon replicas employing stereo-electron microscopy. This enabled comparisons to be made of the roughness formed by each treatment.

Transmission and reflection electron diffraction in an Elmskop-1A (Siemens) electron microscope operating at 100 KV were used to identify the surface materials. When the thin film formed on the alloy surface during the pretreatments was required for examination by transmission it was detached from the substrate using 10% w/v bromine in anhydrous methanol. In some cases the film was strengthened before stripping by depositing Alloprene® (a chlorinated natural rubber product from ICI Ltd.) from chloroform solution on the specimen. Alloprene was later removed from the stripped coating by gentle washing with chloroform.

The technique employed in reflection was that of a glancing angle and therefore only half diffraction rings were obtained. The intensity of diffracted lines obtained by this method varies, among other things, according to their

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position since partial blockage of the diffracted rays is inevitable but their positions are unaffected.

Since it is well established that oxidation of titanium in air at elevated temperatures leads to the formation of a film of rutile, a sample prepared in this way was used to establish the instrumental parameters.

The effects of the following etching solutions were investigated:

- 1) Hydrofluoric acid, 4% w/v at 23°C.
- 2) Hydrochloric acid, 10% w/v at boiling point (103°C).
- 3) Sulphuric acid, 10% w/v at boiling point (103°C).
- 4) Anodising in 0.1 N sulphuric acid for 30 seconds at potentials between 10 and 55 volts.
- 5) Alkaline (sodium hydroxide) solutions of hydrogen peroxide at 23°C.
- 6) Hydrofluoric acid 4% solution followed by immersion in a solution containing trisodium phosphate (5% w/v), sodium fluoride (0.9% w/v) and hydrofluoric acid (1.6% w/v). This treatment is commonly known as phosphate-fluoride treatment.

In each case the etched samples were washed thoroughly with distilled water and rinsed with acetone before they were dried under vacuum.

Typical lattice spacings obtained with IMI-318 alloy as shown in Table I and those for pure titanium are shown in Table II. Figure 1 compares the experimental lattice spacings obtained by treatment with alkaline hydrogen peroxide ("black oxide") and with phosphate-fluoride together with the

TABLE I
Reflection electron diffraction of Ti-6Al-4 V (IMI-318) alloy given various surface treatments.

	Alkaline hydrogen peroxide "black oxide"		Phosphate-fluoride treatment		Hydrochloric acid		Sulphuric acid		Hydrofluoric acid		Anodic oxidation		Air oxidation		ASTM data for TiO ₂ -rutile	
	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o	dÅ	I ^o
1	3.266	vw	3.277	w	3.201	w	3.281	vw	3.218	w	3.295	vw	3.266	w	3.245	100
2	2.455	m/w	2.481	m	2.499	m/w	2.478	m/w	2.509	m/w	2.479	m	2.470	m/w	2.489	41
3	2.278	w	—	—	—	—	—	—	—	—	—	—	—	2.297	7	
4	2.190	m	2.187	m	2.196	m	2.201	m	2.205	m	2.201	m/w	2.177	m/w	2.188	22
5	2.100	w	—	—	2.106	w	2.077	w	2.079	w	2.088	w	—	—	2.054	9
6	1.688	st	1.689	st	1.691	st	1.679	st	1.699	st	1.695	st	1.687	st	1.687	50
7	1.622	m	1.622	w	1.620	w	1.619	w	1.608	w	1.633	w	1.642	m	1.624	16
8	1.470	vw	—	—	1.476	w	1.477	w	1.459	w	1.478	vw	1.468	w	1.480	8
9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.453	6
10	1.370	w	1.355	w	1.361	w	1.358	w	1.360	vw	1.359	vw	1.350	vw	1.360	16
11	—	—	—	—	1.340	w	1.348	w	1.350	w	—	—	1.335	vw	1.347	7
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

^o Intensity.

A.S.T.M. data for the titanium oxides. No lines due to brookite, anatase, hydride, fluoride or phosphate were seen in any of the specimens examined. Selective area diffraction was employed on stripped oxide coatings using bromine methanol solution, and even this technique failed to show any diffraction lines apart from those of rutile.

TABLE II
Reflection electron diffraction examination of titanium (IMI-115) surface given various treatments

	Alkaline hydrogen peroxide "black oxide"		Phosphate-fluoride treatment		Hydrochloric acid		Sulphuric acid		Hydrofluoric acid		Anodic oxidation		Air oxidation		ASTM data for TiO ₂ -rutile	
	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a	dÅ	I ^a
1	3.258	vw	3.255	vw	3.249	vw	3.288	vw	3.288	vw	3.256	vw	3.248	vw	3.245	100
2	2.466	m/w	2.477	m	2.488	m	2.477	m/w	2.478	m	2.477	m	2.466	m	2.489	41
3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.297	7
4	2.200	m	2.189	m	2.177	m	2.187	m	2.193	m	2.180	m	2.205	m	2.188	22
5	2.107	vw	—	—	—	—	—	—	—	—	2.093	vw	2.089	vw	2.054	9
6	1.677	st	1.677	st	1.688	st	1.688	st	1.689	st	1.677	st	1.688	st	1.687	50
7	1.628	w	1.620	w	1.619	w	1.628	w	1.623	w	1.644	w	1.652	w	1.624	16
8	1.488	vw	1.444	vw	1.452	vw	—	—	1.500	vw	—	—	1.510	vw	1.480	8
9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.453	6
10	1.355	w	1.360	w	1.344	w	1.380	vw	1.349	w	1.355	w	1.368	w	1.360	16
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

^a Intensity.

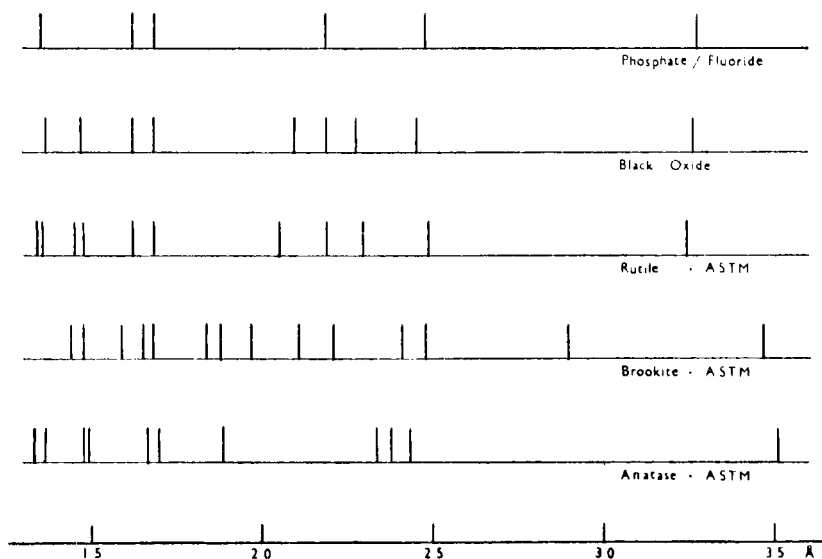


FIGURE 1 X-ray powder diffraction data comparison

Clearly whichever pretreatment is used, rutile is the only crystalline oxide formed on the surface. However, selective area diffraction and transmission techniques showed that the degree of crystallinity was different for each treatment.

Crystallinity, judged by the sharpness of the diffraction lines, decreased according to the treatment in the following order:

alkaline hydrogen peroxide; phosphate-fluoride; hydrofluoric acid; anodic oxidation; hydrochloric acid; sulphuric acid.

Stereo-electron microscopy was used to examine the surfaces obtained by the treatments, all of which lead to a more or less rough surface except anodic oxidation which simply reproduces the initial surface of the metal. Even when prolonged electrolysis is used no change occurs in the surface topography. The final condition of the surfaces produced are illustrated in Figures 2-7.



FIGURE 2 IMI 318 alloy etched with hydrofluoric acid 4% at 23°C for 1½ minutes. Original magnification $\times 2500$.

The alkaline decomposition of hydrogen peroxide is a rather special case since it depends upon three factors; the ratio and the concentrations of the reagents as well as the length of oxidation time. This treatment was studied by Bianchi, Mazza and Trosatti⁵ who showed that while at higher concentrations of peroxide or alkali or both, passivation or extensive corrosion occurred, at intermediate concentrations coloured oxide coatings were produced. The colour of these coatings varies from yellow through blue and



FIGURE 3 IMI 318 alloy etched with hydrochloric acid 10% at 103°C for 45 minutes. Original magnification $\times 2500$.



FIGURE 4 IMI 318 alloy etched with sulphuric acid 10% at 103°C for 45 minutes. Original magnification $\times 2500$.

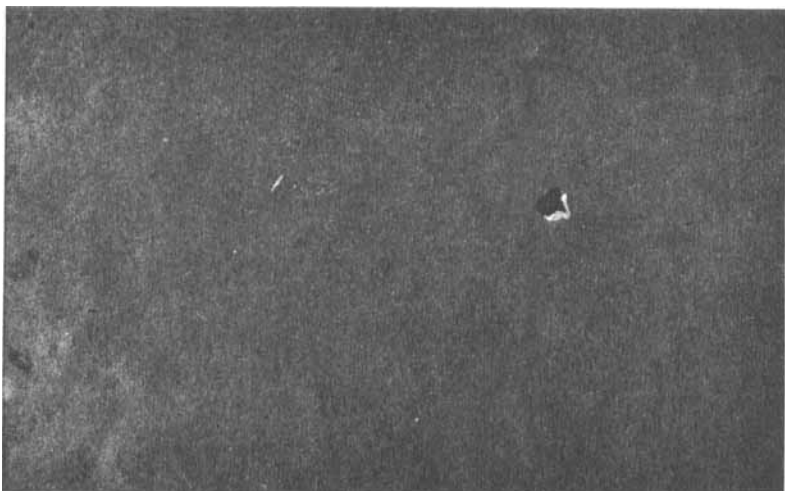


FIGURE 5 IMI 318 alloy anodised in sulphuric acid 0.1 *N* at 50 volts for 30 seconds. Original magnification $\times 2500$.

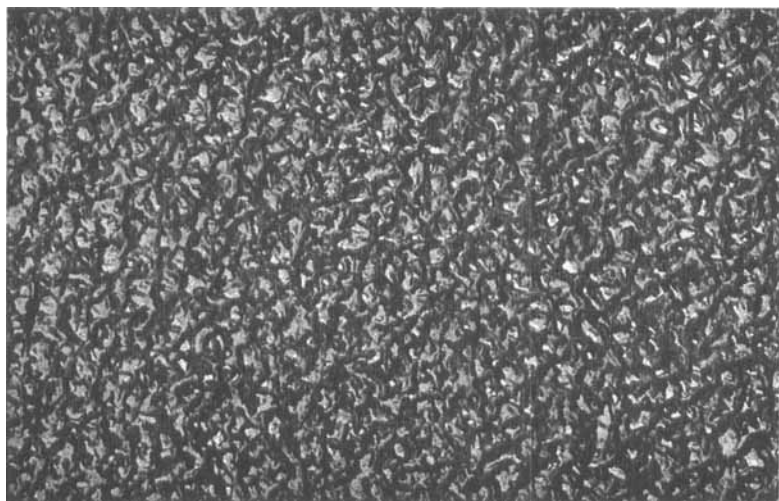


FIGURE 6 IMI 318 alloy etched in sodium hydroxide 0.40 *M*. solution of hydrogen peroxide 0.05 *M* at 23°C for one hour. Original magnification $\times 2500$.



FIGURE 7 IMI 318 alloy phosphate-fluoride treatment for 3 minutes. Original magnification $\times 2500$.

All these photographs are of the same magnification and strictly comparable.

mauve to grey and black, and the surface roughness varied with the colour. The roughest and most satisfactory for bonding were the black coloured surfaces produced in 1–2 hours of treatment at room temperature. Longer periods of oxidation resulted in less crystalline and very porous surfaces.

CONCLUSIONS

For efficient adhesive bonding, a surface coated with a stable oxide in a coherent and rough form is necessary. The character of this roughness must be such that the crevices are easily filled by the adhesive flowing in without trapping gas bubbles.⁶ As can be seen from the illustrations, the surface produced by short periods of oxidation in alkaline hydrogen peroxide solution under conditions which yield black oxide fulfils these requirements. The effects of these various surface pretreatments on adhesive bond strengths are discussed in detail elsewhere.^{7, 8}

Here it is sufficient to say that these conclusions about the optimum surface for bonding are in accord with the results there described.

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