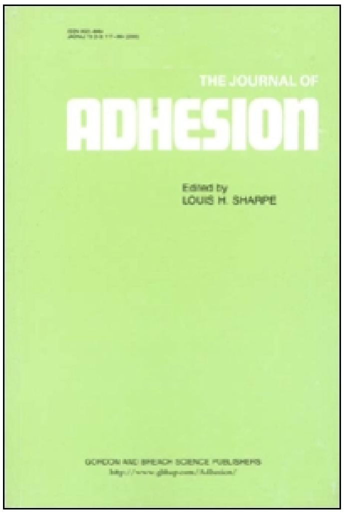
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Comment on "Sodium Hydroxide Anodization of Ti-6AI-4V Adherends", {J. Adhesion 20,283 (1987)}

H. M. Clearfield[a]; G. D. Davis[a]
[a] Martin Marietta Laboratories, Baltimore, Maryland, U.S.A.

To cite this Article Clearfield, H. M. and Davis, G. D.(1987) 'Comment on "Sodium Hydroxide Anodization of Ti-6AI-4V Adherends", {J. Adhesion 20,283 (1987)}', The Journal of Adhesion, 24: 2, 221 — 225
To link to this Article: DOI: 10.1080/00218468708075428
URL: http://dx.doi.org/10.1080/00218468708075428

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1987, Vol. 24, pp. 221–225
Photocopying permitted by license only
© 1987 Gordon and Breach Science Publishers, Inc.
Printed in the United Kingdom

Comment on "Sodium Hydroxide Anodization of Ti-6Al-4V Adherends," {J. Adhesion **20**, 283 (1987)}

H. M. CLEARFIELD and G. D. DAVIS

Martin Marietta Laboratories 1450 South Rolling Road Baltimore, Maryland 21227 U.S.A.

Downloaded At: 15:36 22 January 2011

(Received April 20, 1987; in final form May 22, 1987)

The recent article "Sodium Hydroxide Anodization of Ti-6A1-4V Adherends" by Filbey, Wightman and Progar[1] is commendable in that a wide variety of analytical techniques has been used to study the surface preparation first reported by Kennedy, Kohler and Poole.[2] We too have conducted in-depth studies of surface preparations for Ti-6A1-4V adherends with recent emphasis on chromic acid and sodium hydroxide anodization (CAA and SHA, respectively). Our initial results were in agreement with those presented by Filbey *et al.* (hereafter "the authors") regarding surface composition and oxide sputter-etching efficiency. However, the results of more detailed work have shown that these observations (and the subsequent conclusions) may be influenced by instrumentation effects. We wish to highlight these briefly.

We have studied both the SHA and the CAA oxides using high-resolution X-ray photoelectron spectroscopy (XPS). To determine the oxide stoichiometry, we used sensitivity factors derived individually from high-resolution spectra of unsputtered anatase and rutile powders—both phases were verified separately by X-ray diffraction. (In both powders, less than 3% of the oxygen present at the surface could be associated with adventitious carbon.) The

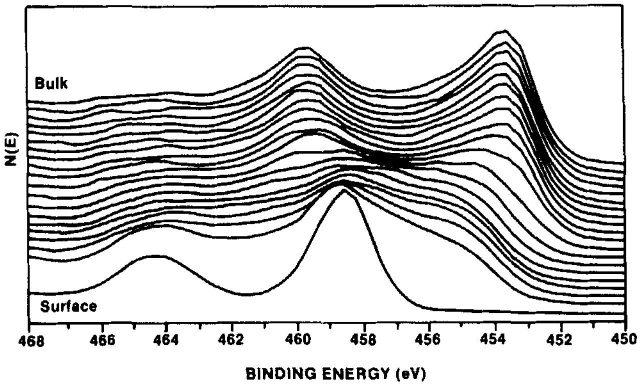


FIGURE 1 High-resolution XPS spectra of the Ti 2p photoelectron states as a function of depth through the SHA oxide. Each scan represents ~10 nm removed by sputter etching. The surface is at the front.

Downloaded At: 15:36 22 January 2011

sensitivity factors attained in this manner were subsequently confirmed by high-resolution spectra of TiO powder. Using these, we obtained an O/Ti ratio of 2.0 ± 0.1 for several as-anodized samples of both SHA and CAA oxides, indicative of stoichiometric TiO_2.

The importance of using unsputtered TiO_2 standards to determine the sensitivity factors must be stressed because Ti-oxide powders[3] and Ti-adherend oxides[4] are sputter reduced by energetic Ar^+ ions under typical experimental conditions. This is demonstrated in Figure 1,[4] a series of high-resolution spectra of the Ti 2p bound state recorded as a function of depth through an SHA oxide. Each scan corresponds to ~10 nm removed. The surface spectrum (before ion bombardment) consists of a single oxidation state that we assign to TiO_2. As the SHA oxide is sputter etched for the first 70 nm, it becomes difficult to distinguish any oxidation state of Ti—the photoelectron distribution is essentially a "window" ~13 eV wide. (We observed a similar sputter-induced reduction of TiO_2 powder.) After 90 nm is removed, a single, distinguishable bound state emerges from this window. This state is 4.9 eV below that observed at the surface and corresponds to metallic Ti (see below). Therefore, we conclude again that our SHA oxide is TiO_2, and note that it is reduced readily by energetic ions and, possibly, by electrons.[5,6]

TABLE I
Binding energy of the Ti $2p_{3/2}$ photoelectron as a function of oxidation state, from Ref. 7

Oxidation state	Binding energy (eV)
Ti (elemental)	454.0
TiN	455.7
TiO	455.0
TiO_2	458.7

The authors' high-resolution XPS binding energy results, which are not discussed in the text but are listed in Table I (p. 289), are in agreement with ours. In their table, the Ti $2p_{3/2}$ binding energy is given as 458.3–458.8 eV (referred to the C 1s bound state at 285.0 eV). Based on literature values[7] of binding energies for Ti $2p_{3/2}$ electrons in various oxidation states, which are given in our Table I, and referenced to the authors' C 1s level, the $2p_{3/2}$ photoelectron for TiO would occur at 455.0 eV and that for TiO_2 at 458.7 eV. Thus, the authors should have assigned the TiO_2 oxidation state to the Ti $2p_{3/2}$ transition reported in their Table I.

The assignment of TiO_2 would also be in better agreement with the authors' reported surface compositions. In their Table I, the O/Ti ratio ranges from 2.7–5.4, but is calculated from the listed atomic concentrations to be 4.1–10.6. In all cases, the O/Ti ratio is too high; some oxygen is likely to be associated with contamination, but it cannot explain all of the excess. Although large variations in intensity ratios have been reported for large-scale round robins,[8] results from a single research group should be internally consistent to within 50%, even from uncalibrated instruments. Neither these discrepancies nor the differences between measurements taken with the different instruments are explained.

The authors' use of Auger electron spectroscopy (AES) to determine the oxidation state of Ti should be equally as valid as XPS, but AES has less sensitivity to mixtures of chemical states[3] such as an SHA (or any TiO_2) surface that has been sputter etched (our Figure 1). XPS measurements preclude the assignment of a distinct chemical state for Ti in the sputter-etched oxide. Auger lineshape measurements of the Ti LMM and LMV transitions made on CAA oxides that were sputter etched for up to six-minute intervals were indicative of Ti_2O_3 and/or TiO.[3] Such an assignment

Downloaded At: 15:36 22 January 2011

Downloaded At: 15:36 22 January 2011

is likely to be an averaged stoichiometry, however. If such a single chemical state did exist in the sputter-etched oxide, high-resolution XPS measurements would have detected it.

The authors' statement that the SHA oxide cannot realistically be 20 times thicker than the CAA oxide is indeed valid. However, we can see no reason why an SHA oxide would sputter etch with less efficiency than a CAA oxide. As can be seen in our Figure 1, metallic Ti can be detected after 90 nm of oxide has been removed even though the "window" due to sputter-induced reduction persists. This is strictly an instrumental effect due to the ion gun/electron analyzer geometry,[4] *i.e.*, in some areas the ion beam is shadowed due to the large, mountainous features created during anodization (see authors' Figure 1). Because the ion gun and electron analyzer are not coaxial, the analyzer samples uneroded areas, giving rise to an apparent oxide signal. A rough estimate of the oxide thickness can be obtained from Figure 1 by noting the depth at which the Ti metallic state first appears. However, a better method is to use scanning Auger microscopy (SAM) to profile the relatively large, flat regions between the "mountains." In this case, the sample can be tilted to expose the flat areas to the ion beam and the incident electron beam can be focussed precisely enough to illuminate only those areas. We have done this for the flat areas of several SHA oxides and the oxide thickness values we obtain, *i.e.*, 80–90 nm, are in good agreement with that derived from Figure 1.[4]

Our intent in writing this comment has been to strengthen some of the conclusions and to resolve (in what we believe to be the most timely fashion) some of the issues raised by Filbey *et al.* We intend to address these and other issues in more detail at a later date.[4]

References

1. J. A. Filbey, J. P. Wightman, and D. J. Progar, *J. Adhes.* **20,** 283 (1987).
2. A. C. Kennedy, R. Kohler, and P. Poole, *Int. J. Adhes. Adhesives* **3,** 133 (1983).
3. G. D. Davis, K. A. Anderson, and M. Natan, *Appl. Surf. Sci.* **15,** 321 (1983).
4. H. M. Clearfield, G. O. Cote, K. A. Olver, D. K. Shaffer, and J. S. Ahearn, presented at the 9th Symposium on Applied Surface Analysis, Dayton, OH, 3–5 June, 1987 (Proceedings to appear in *Surface and Interface Analysis*).
5. S. Thomas, *Surf. Sci.* **55,** 754 (1976).
6. H. J. Mathieu, J. B. Mathieu, D. E. McClure, and D. Landolt, *J. Vac. Sci. Technol.* **14,** 1023 (1977).

7. D. Briggs, in *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy,* D. Briggs, and M. P. Seah, Eds. (Wiley, Chichester, UK, 1983), p. 359.
8. C. J. Powell, N. E. Erickson, and T. E. Madey, *J. Electron Spectrosc. Relat. Phenom.* **17,** 361 (1979).

Downloaded At: 15:36 22 January 2011