

## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

NASA Technical Memorandum 79117

(NASA-TM-79117) ADHERENCE OF SPUTTERED  
TITANIUM CARBIDES (NASA) 10 p HC A02/MF A01  
CSCL 11F

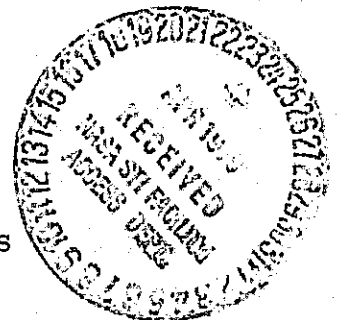
N79-20220

G3/26 19447  
Unclas

ADHERENCE OF SPUTTERED  
TITANIUM CARBIDES

William A. Brainard and Donald R. Wheeler  
Lewis Research Center  
Cleveland, Ohio

TECHNICAL PAPER to be presented at the  
International Conference on Metallurgical Coatings  
San Diego, California, April 23-27, 1979



# ADHERENCE OF SPUTTERED TITANIUM CARBIDES

by William A. Brainard and Donald R. Wheeler

National Aeronautics and Space Administration

Lewis Research Center

Cleveland, Ohio

## INTRODUCTION

E-9950

There is now a large amount of information in the literature on the sputter deposition of refractory compounds and particularly titanium carbide (TiC) onto steel. In all cases a substrate bias voltage has been required to reduce oxide impurities and improve the compound stoichiometry in the film proper (refs. 1 and 2). However, the resultant decrease in the concentration of oxides in the interface between substrate and coating has resulted in poor adhesion of the coating (ref. 2). Therefore, oxidation of the substrate (ref. 3) or of the interfacial region by reactive sputtering (refs. 3 and 4) have been used to enhance the adhesion of TiC and other refractory metal compounds to steel substrates. Further investigation (ref. 5) showed that oxidation of the interface did not result in the best adhesion of TiC to steel. A mixed nitride interface, formed by reactive sputtering in nitrogen, was much more effective. It could not be assumed, therefore, that oxidation would be the most effective interface treatment for alloys of metals other than iron.

The objective of the present investigation was to search for interface treatments that would increase the adhesion of TiC to nickel and titanium based alloys. The alloys Ti-6Al-4V (6 wt% Al, 4 wt% V, balance Ti) and René 41 (19 wt% Cr, 11 wt% Mo, 3 wt% Ti, balance Ni) were chosen as representatives of their types. Adhesion of the coatings was evaluated in pin-and-disk friction tests. The coatings and interface regions were examined with X-ray photoelectron spectroscopy (XPS).

## EXPERIMENTAL

The alloys were commercial materials of the nominal composition given above. They were cast in the form of disks 6.4 cm in diameter and 1.3 cm thick. One flat face of the disks which was to be coated, was finished by grinding on SiC papers polished with diamond polish, and finished with 1  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ . The TiC sputtering target was a commercial hot-pressed compact. A cast Ti metal target was also used.

The coatings were applied in an rf-sputtering apparatus which has been described before (ref. 2). Target power density was 1.64  $\text{W}/\text{cm}^2$  with deposition times from 5 to 40 minutes. The shorter times were used to make thin specimens for XPS analysis. The sputtering atmosphere could be controlled by admitting gas during sputtering through two leak valves. The sputtering pressure was kept at about 2.7  $\text{N}/\text{m}^2$  (20  $\mu$ ). The disk could be biased with a dc voltage. Before deposition, the targets were cleaned by rf-sputtering until there was little pressure rise due to outgassing. The disk specimen was sputter etched, if desired, at -1200 V in 2.7  $\text{N}/\text{m}^2$  of argon for 15 minutes. The system was then evacuated, the appropriate initial sputtering atmosphere established, and a bias voltage of -500 or -1000 V was applied to the disk. After intervals from a few seconds to 30 minutes, the bias voltage was set at -500 V, rf power was applied to the target, and the disk was moved under the target to begin deposition. Two minutes later the sputtering atmosphere was reduced to pure argon and the deposition completed.

The coated disks were tested in the friction apparatus which has been described in detail elsewhere (ref. 6). A 304-SS hemisphere (0.95 cm diam) was loaded against the coated disk while it rotated. The sliding speed of the disk under the rider was 25 cm/s. Tests were performed in a dry nitrogen atmosphere at room temperature and lasted 30 minutes. The load was varied from 0.1 to 2.0 N. Failure of the coating by spalling caused a sudden increase in the coefficient of friction and rapid wear of the 304-SS rider and of the underlying substrate. If the coating adhered, the friction was steady and low and no wear was detectable in profilometer traces of the wear tracks.

The coatings were analyzed with XPS as in earlier studies (refs. 2 and 7). Peaks in the XPS spectrum identify the elements present and can indicate their oxidation state. The size of the peak is related to the amount of the element present in the analyzed volume, which extends to about 20 Å below the surface. By repeatedly sputter etching the coating with an ion-gun (5 keV argon ions) and analyzing with XPS, depth profiles of the films could be created. These showed the material composition as a function of depth below the surface. The rate of sputter etching measured on TiC samples of known thickness was about 5 Å per minute.

## RESULTS AND DISCUSSION

### René 41 Substrate

When heated in air at 550° C the surface of René 41 first forms a thin Cr<sub>2</sub>O<sub>3</sub> layer (after about 24 hr), then a layer of NiO forms over the Cr<sub>2</sub>O<sub>3</sub> (after about 120 hr) (ref. 8). TiC was rf sputter deposited onto disks with each of these oxide surfaces as well as onto a sputter etched disk. Another disk was coated using a partial pressure of acetylene ( $5 \times 10^{-5}$  torr) during the first two minutes of deposition. Figure 1 shows that all the coatings performed reasonably well at 0.5 N load, but only the one reactively sputtered in acetylene did not fail at 1.0 N. Profilometer traces confirmed that this coating showed no wear, while the others had spalled. Coatings prepared using a higher partial pressure of acetylene ( $1 \times 10^{-4}$  torr) peeled spontaneously and could not be tested.

Samples of René 41 were then prepared by sputtering in two different partial pressures of acetylene at two different bias voltages but without depositing TiC. These samples were analyzed with XPS after sputter etching for 1 minute to remove surface contamination. Table I shows that the amount of carbon on the surface depends on both the partial pressure of acetylene and the bias voltage.

The C(1s) peak was generally composed of two separate peaks one at 284.5 eV binding energy which is associated with graphite carbon (ref. 9), and another at 283.2 eV which was due to a metal carbide (ref. 10). Depth profiles (fig. 2) of the -1000 V bias specimens prepared at  $1 \times 10^{-4}$  and  $5 \times 10^{-5}$  T showed that the surface

of the former was predominantly graphite while the latter was mainly carbide. A carbide interface seemed to produce good adhesion of TiC to René 41 while a graphite containing interface caused extremely poor adhesion.

#### Ti-6Al-4V Substrate

Four different surface treatments for the titanium alloy substrate were examined. Figure 3 shows that neither sputter etching, oxidizing in air, nor forming the interface in a nitrogen containing sputtering atmosphere, produced coatings that adhered well at loads of 0.1 N. The profilometer traces show that high substrate wear occurred because of spalling of the TiC coating. Figure 4(d) presents the result of a test on a coating formed by sputter depositing a layer of metallic Ti about 300 Å thick onto a sputter etched Ti-6Al-4V substrate just before depositing the TiC coating. There is no wear and the friction is low. Such coatings were tested successfully at loads up to 1.0 N.

The Ti interlayer was tried because it was suspected that the Ti-6Al-4V might have a passive  $\text{Al}_2\text{O}_3$  layer that inhibited adhesion. To investigate this possibility further, depth profiles of TiC on sputter etched Ti-6Al-4V were compared to depth profiles of TiC coatings with a Ti interlayer (fig. 4). Because the depth profiles are complex, the interpretation of figure 4 is difficult. We do observe, however, that aluminum oxide is predominant in the interface next to the coating when no Ti interlayer is used, while in the other case the aluminum metal occurs next to the coating along with excess Ti, as would be expected. It appears that the Ti metal is able to form an adherent film on the  $\text{Al}_2\text{O}_3$  passive layer and at the same time provide a good substrate for the TiC coating.

#### CONCLUSIONS

When the results for the René 41 substrate are evaluated along with previous results for TiC on steel (refs. 4 and 5) and for several molybdenum compounds on steel (ref. 3), one is led to think that sputtered refractory compound coatings adhere best when a mixed compound of coating and substrate metals is formed in the

interfacial region. This is consistent with observations that spinel formation enhances the adhesion of metal films to oxides (refs. 11 to 15). The most effective type of refractory compound interface appears to depend on both substrate and coating material. Furthermore, the results on René 41 illustrate the sensitivity of the interface to process parameters.

The Ti interlayer on Ti-6Al-4V is effective in an entirely different way than the mixed compound layers in the other cases. This suggests that a combination of the two mechanisms, metallic interlayer deposition and mixed compound interface formation may be more effective for some substrate coating combinations than either alone.

#### REFERENCES

1. J. L. Vossen, J. Vac. Sci. Technol., 8 (1971) 751.
2. D. R. Wheeler and W. A. Brainard, J. Vac. Sci. Technol., 15 (1978) 24.
3. W. A. Brainard and D. R. Wheeler, J. Vac. Sci. Technol., 15 (1978) 1800.
4. J. E. Greene and J. L. Zilko, Surf. Sci., 72 (1978) 109.
5. W. A. Brainard and D. R. Wheeler, J. Vac. Sci. Technol., 16 (1979).
6. W. A. Brainard and D. R. Wheeler, NASA Tech. Paper 1377, 1979.
7. D. R. Wheeler and W. A. Brainard, NASA Tech. Paper 1161, 1978.
8. D. R. Wheeler, NASA Tech. Memo. TM-78839, 1978.
9. J. W. Robinson, ed., Handbook of Spectroscopy, Vol. 1, CRC Press, Cleveland, 1974.
10. D. R. Wheeler and W. A. Brainard, NASA Tech. Paper to be published, 1979.
11. A. R. Blackburn, T. S. Shevlin, and H. R. Lower, J. Am. Ceram. Soc., 32 (1949) 81.
12. G. Katz, Thin Solid Films, 33 (1976) 99.
13. T. E. O'Brien and A. C. D. Chaklades, J. Am. Ceram. Soc., 57 (1974) 329.
14. S. V. Pepper, J. Appl. Phys., 47 (1976) 801.
15. D. M. Mattox, J. Appl. Phys., 37 (1966) 3613.

TABLE I. - C(1s) XPS PEAK HEIGHTS

(ARB. UNITS) AFTER 1 min

## SPUTTER ETCH

Bias voltage	Partial pressure of acetylene, torr	
	$1 \times 10^{-4}$	$5 \times 10^{-5}$
-500	2250	600
-1000	4600	1170



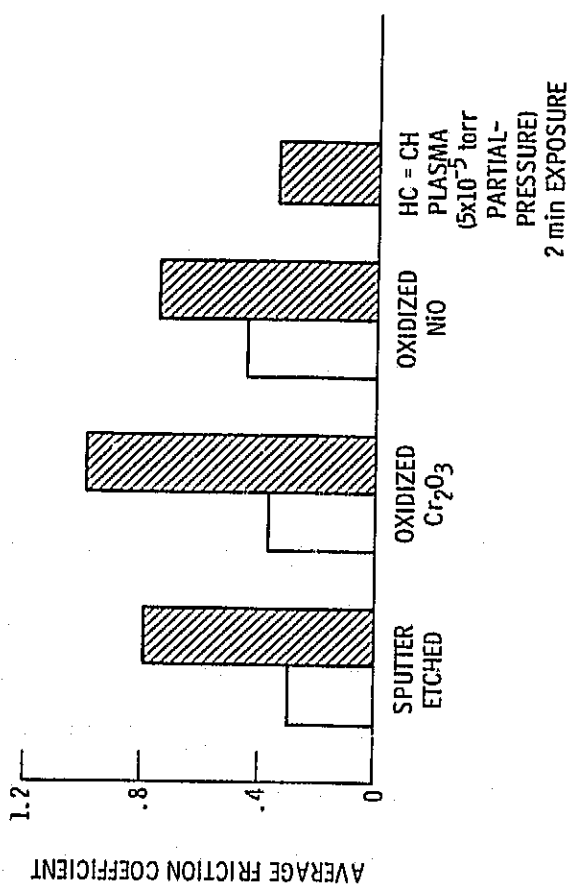
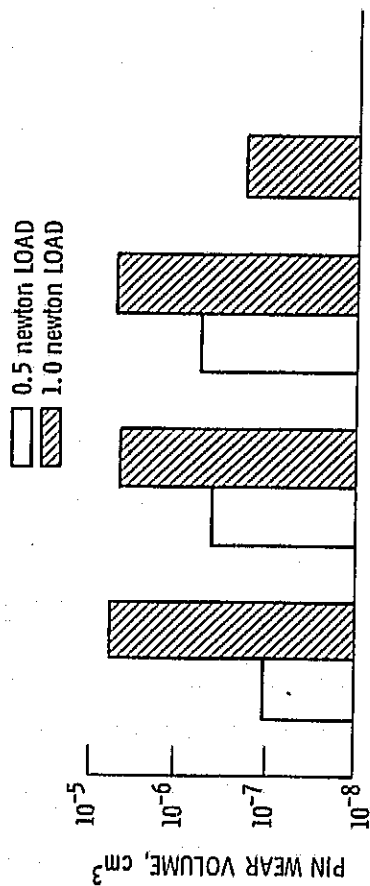


Figure 1. - Friction and wear for TiC coated René 41 - AISI 304 stainless steel rider, 25 cm/s sliding speed, 30 min run, nitrogen atmosphere, room temperature.

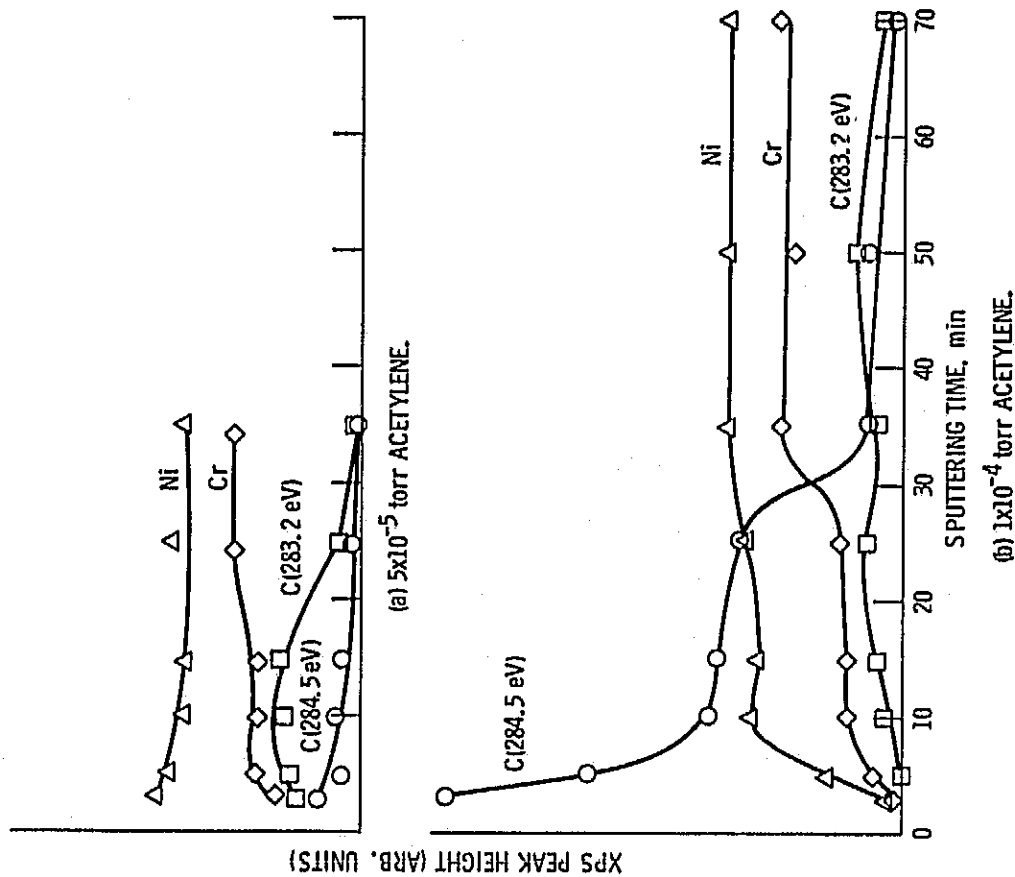


Figure 2. - XPS depth profiles of René 41 sputtered in C<sub>2</sub>H<sub>2</sub> containing atmosphere - 1000 V for 2 minutes. Depth profiling rate approximately 5 Å/min.

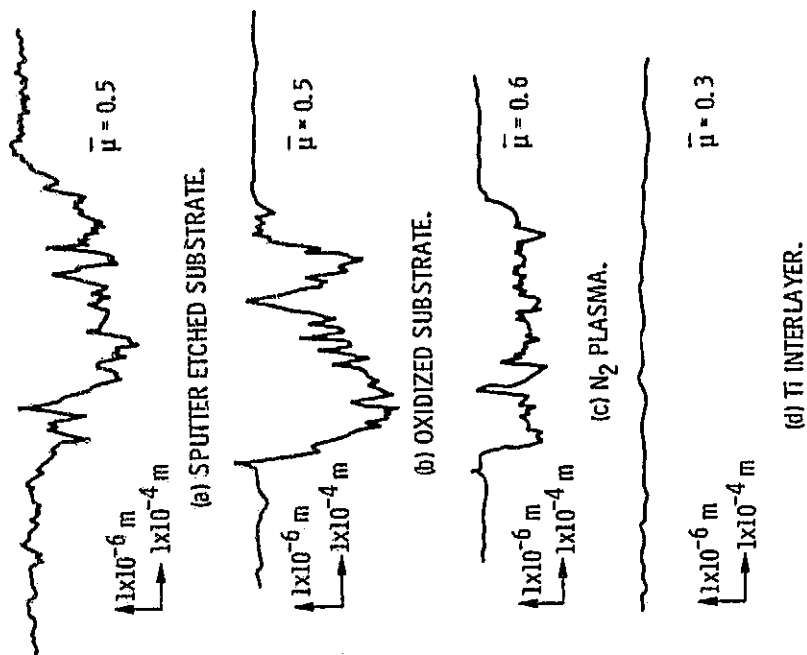


Figure 3. - Surface profilometer traces of wear tracks on TiC coated Ti-6Al-4V - AISI 304 SS rider, 25 cm/s sliding speed, 30 min run, nitrogen atmosphere, room temperature.

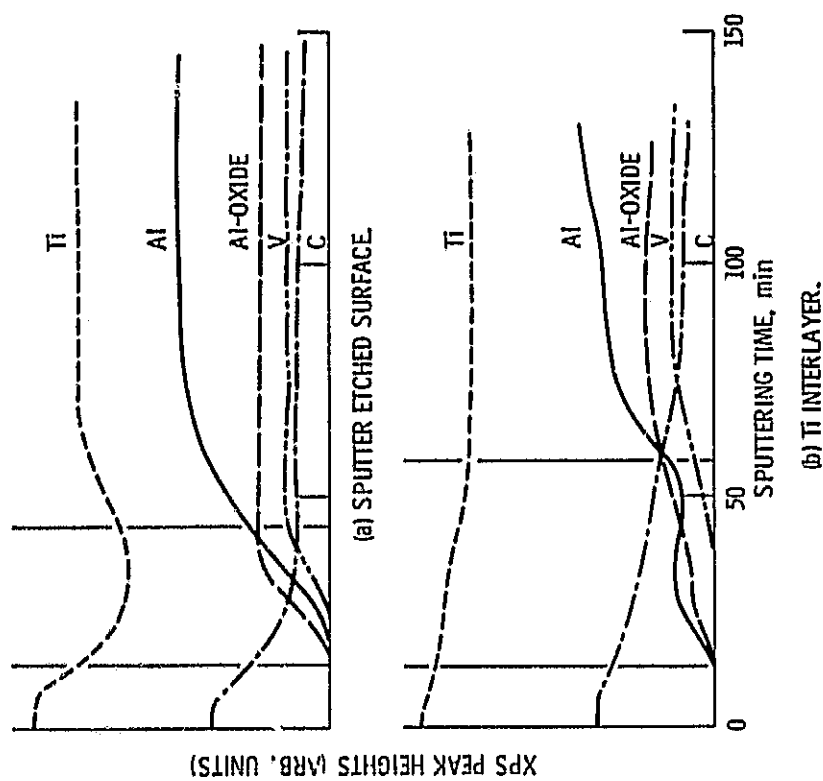


Figure 4. - XPS depth profiles of TiC coated Ti-6Al-4V - depth profiling rate approximately 5 Å/min.