



ELSEVIER

Surface Science 481 (2001) 185–197

SURFACE SCIENCE

www.elsevier.nl/locate/susc

# Chemical modification of the interfacial frictional properties of vanadium carbide through ethanol adsorption

B.I. Kim <sup>a</sup>, S. Lee <sup>a</sup>, R. Guenard <sup>a</sup>, L.C. Fernandez Torres <sup>a</sup>, S.S. Perry <sup>a,\*</sup>,  
P. Frantz <sup>b</sup>, S.V. Didziulis <sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Houston, Houston, TX 77240-5641, USA

<sup>b</sup> Department of Materials Science, Space Materials Laboratory, The Aerospace Corporation, El Segundo, CA 90245, USA

Received 8 January 2001; accepted for publication 19 March 2001

## Abstract

The frictional properties of the (1 0 0) face of vanadium carbide have been measured with atomic force microscopy (AFM) as a function of ethanol exposure under ultrahigh vacuum conditions. Although exhibiting a small sticking coefficient, ethanol reacts upon adsorption at room temperature producing a thin chemisorbed layer. This reaction has been characterized through high resolution electron energy loss spectroscopy and temperature programmed desorption. These studies demonstrate the formation of a partially dehydrated species involving bonds to the surface through both oxygen and carbon atoms. The growth of this reaction layer film has been followed with X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and scanning tunneling microscopy. The results of these surface analytical measurements have been correlated with the frictional and adhesion properties measured with AFM. An approximate 40% reduction in frictional forces is observed upon the formation of a complete monolayer of a hydrocarbon reaction layer. Little change in the interfacial friction was detected at higher or lower exposures of ethanol. The origin of the friction reduction, which cannot be directly related to changes in interfacial adhesion, is assigned to a change in interfacial shear strength as a result of the growth of the ethanol decomposition species. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Atomic force microscopy; Tribology; Surface chemical reaction; Lubrication; Carbides; Alcohols; Low index single crystal surfaces

## 1. Introduction

Vanadium carbide (VC) belongs to a class of materials that possess high melting points and very high hardness and wear resistance. It has also been

demonstrated that these materials can be deposited as thin films by a number of techniques [1–6]. As a result, metal carbides are now employed in a number of applications where thin carbide films serve as wear-resistant protective coatings [7]. In many of these applications, the tribological interface is made up of three bodies including the coating surface, a lubricating medium, and the counterface. In these settings, the chemical reactivity of the carbide surface towards atmospheric

\* Corresponding author. Tel.: +1-713-743-2715; fax: +1-713-743-2709.

E-mail address: perry@uh.edu (S.S. Perry).

and lubricant species plays a central role in determining the performance and stability of the tribological interface.

In previous studies, we have reported the interfacial frictional properties of metal carbides and nitrides under ambient conditions and the frictional properties of VC under vacuum conditions as a function of oxygen exposure [8,9]. These studies have used atomic force microscopy (AFM) to measure the frictional properties of well-characterized carbide and nitride surfaces in contact with a single microasperity, namely the AFM tip. In the present study, we have explored the frictional properties of single crystal VC under vacuum conditions as a function of exposure to molecular ethanol. The complete chemical characterization of the temperature-dependent surface reaction of ethanol with VC is being reported elsewhere [10]. In this paper we focus on the room temperature adsorption and reaction of ethanol and the consequent modification of frictional properties. In these studies ethanol is intended to model alcohol and ether functionalities encountered in both lubricants and lubricant additives.

Our study has taken the approach of following changes in the surface composition and morphology with techniques including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS) as a function of ethanol exposure under ultrahigh vacuum (UHV) conditions. The interaction of ethanol with the VC(100) surface has also been characterized through high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). As described above, the frictional and interfacial adhesion properties have been measured with AFM. The advantages of this approach include the opportunity to correlate tribological results with chemical and structural information derived from other surface analytical techniques and to characterize the inherent tribological properties of this carbide surface on a molecular scale in the wearless regime of friction.

The results of these correlated measurements portray the formation of a thin reaction layer (boundary layer) composed of partially dehydrated ethanol. This reaction layer exhibits a novel

growth mode below a monolayer coverage and is observed to nucleate at the step edges of the single crystal VC surface. Within the first layer, the reaction layer has been characterized as possessing the same C:O stoichiometry as molecular ethanol, however the film becomes carbon rich at higher exposures. An abrupt change in the interfacial friction of the VC surface is observed with the completion of the first layer of the reaction film. These changes in interfacial friction cannot be correlated to changes in interfacial adhesion (although modest and slowly varying adhesion forces are measured with ethanol exposure) or changes in the interfacial electronic structure as observed with oxygen uptake. Instead, the results of this study collectively support the picture of interfacial friction being reduced through the formation of a hydrocarbon film, inherently possessing a lower interfacial shear strength.

## 2. Experimental

The VC samples used in these experiments were obtained from Linfield Research Institute, Linfield College, McMinnville, OR. Experiments performed at the University of Houston and The Aerospace Corporation employed separate (100) oriented single crystals of VC prepared from the same boule. Although, the experiments were not performed on the same sample, independent XPS measurements carried out at both locations verified identical 1:1 V:C surface stoichiometries and cleanliness. The surface of the VC(100) single crystal was prepared for all of these studies through a series of Ar<sup>+</sup> sputter and annealing cycles in UHV. The sample was sputtered for 15 min at room temperature with Ar<sup>+</sup> ions with an accelerating potential of 1 kV and sample current  $I_s \sim 6 \mu\text{A}/\text{cm}^2$ . Following this treatment, the sample was annealed by a combination of radiative and electron beam heating to 1200°C under UHV conditions for 5 min. Ethanol (McCormick Distilling Co. Inc. 99.99%) exposures for the AFM, STM, XPS, and UPS measurements were accomplished by backfilling the entire chamber through a variable leak valve for specific amounts of time.

The STM/AFM experiments have been performed in a UHV chamber housing an Omicron microscope capable of measuring topography, normal force, and lateral force images. The system is also equipped with an Omicron reverse view LEED/Auger system that allowed the determination of surface structure and cleanliness [9,11]. The STM topography measurements were performed using a Pt tip prepared by electron bombardment heating. The interfacial friction and adhesion measurements were carried out with a silicon nitride probe tip (Digital Instruments: V-shaped  $\text{Si}_3\text{N}_4$  contact mode cantilever #4), which possessed a tip radius of 200–300 Å. Normal force values were calculated from the normal deflection of the cantilever using the manufacturer's suggested spring constant ( $k_n = 0.58 \text{ N/m}$ ). Lateral force values were determined using the method outlined by Ogletree et al. [12] and the dimensions of V-shaped cantilever provided by the manufacturer.

The frictional properties of the VC surface were assessed by measuring the normal and lateral forces as the sample was scanned relative to the tip position over a distance of 1000 Å with a scan speed of 4  $\mu\text{m/s}$ . Normal and lateral forces were measured simultaneously as a function of increasing and decreasing applied loads. The frictional force during sliding at a specific load was determined by taking the numerical difference between the left-to-right and right-to-left lateral force scans and dividing by two, i.e. the half-height of the friction loop. This procedure also has the effect of obtaining a spatially averaged frictional force. Subsequently, this frictional force was plotted as a function of load. All of the friction and adhesion measurements were performed with the identical tip/cantilever assembly, thereby insuring the precision of the set of measurements. The maximum load during these experiments was restricted to 30 nN in order to prevent substantial wearing of the tip. The minimum attractive load required to separate the tip from sample surface while sliding as a function of decreasing load is defined here as the pull-off force and is taken to be representative of the adhesion character of an interface.

In a separate UHV system, the TPD, XPS, and UPS spectra of ethanol adsorbed at various cov-

erages on the VC(100) surface were measured. The TPD spectra of ethanol adsorbed at cryogenic temperatures were recorded with a Hiden analytical mass spectrometer over the temperature range of 100–600 K. The details and complete description of the experimental procedures have been reported elsewhere [13]. The influence of ethanol upon room temperature exposure to the VC surface has been followed with XPS and UPS using an Omicron EA125 spectrometer and Vacuum Generators X-ray source ( $\text{MgK}\alpha$ , 1253.6 eV) and UV ( $\text{He(II)}$ , 40.8 eV) sources. The experimental procedures associated with the photoelectron spectroscopy measurements have also been described elsewhere [14]. Finally, in another separate system, the temperature dependent vibrational spectrum of ethanol adsorbed on VC at 150 K has been recorded with HREELS. The details of these measurements are being reported with the TPD measurements described above [10].

### 3. Results

The chemical reaction of ethanol with the VC(100) surface and the subsequent modification of the tribological properties have been studied using an array of surface analytical methods. The interfacial friction and adhesion between a silicon nitride probe tip and the VC surface have been measured with AFM as a function of ethanol exposure at room temperature. The reaction of ethanol with the carbide surface has been studied under two sets of conditions. First, ethanol has been dosed at cryogenic temperatures and then heated to temperatures as high as 600 K. Its adsorption, reaction, and subsequent desorption have been measured as a function of surface temperature with TPD and HREELS and have been described in greater detail in a separate publication [10]. A summary of the results is included below to depict the fundamental nature of the surface reaction of ethanol. Second, the surface reaction has been measured as a function of room temperature exposure of ethanol. Both XPS and UPS have been used to follow changes in the composition of the surface region and the growth of an interfacial reaction layer. Finally, STM and AFM have been

used to follow the topographic and spatial character of the growth of the reaction layer film formed through exposure of the VC surface to ethanol at room temperature. The results of these measurements are described in the following paragraphs.

### 3.1. Tribological properties

The frictional properties of the VC surface have been measured with AFM as a function of ethanol exposure using the procedures described above. In short, the interfacial friction between a silicon nitride probe tip and the VC surface has been measured as a function of both increasing and decreasing load. Typical results of these measurements are shown in Fig. 1A for the decreasing load regime and for a number of ethanol exposures, as well as for the clean VC surface. The modification of the frictional properties through ethanol exposure is evident in these data as the slope of the friction–load plot is reduced with increasing exposure. It should be noted here that relatively large exposures of ethanol were required to induce changes in the frictional properties of the surface as a result of the low sticking probability of ethanol at room temperature. This is apparent from the TPD data presented below. From the data of Fig. 1A and similar sets collected in a number of regions across the sample surface, the average interfacial friction measured at 10 nN is plotted as a function of ethanol exposure (Fig. 1B, filled symbols). An additional characterization of the tip–sample interaction is obtained by determining the force required to separate the tip from the surface during the decreasing load regime of friction measurements. This force is defined here as adhesion and is plotted as a function of ethanol exposure in Fig. 1B (open symbols). While both the interfacial friction and adhesion are observed to decrease with increasing ethanol exposures, both the magnitude and the standard deviation of friction exhibit a noticeable discontinuity above  $\sim 1000$  L. Insight into the origins of this behavior has been obtained through the characterization of interfacial composition and structure as described below.

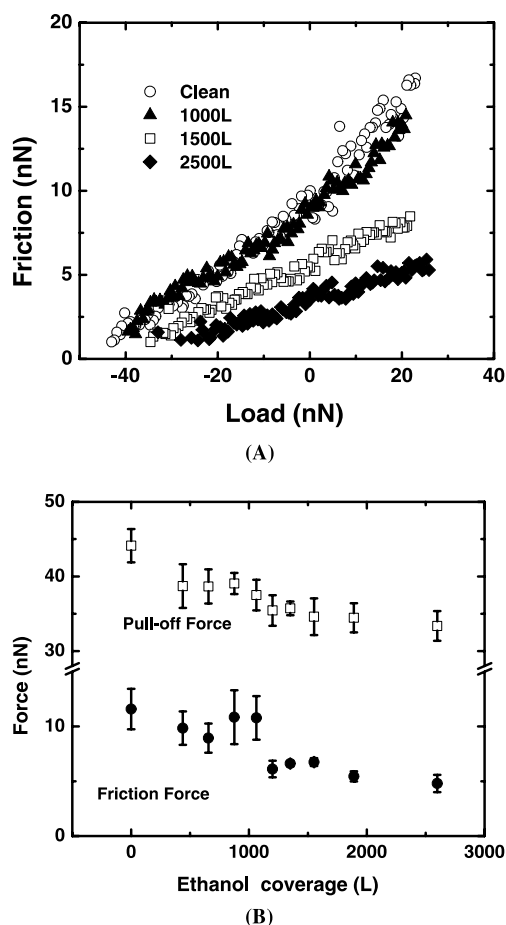


Fig. 1. (A) Friction–load plots measured with AFM under UHV conditions between a silicon nitride probe tip and the VC(100) surface exhibited a reduction in slope with increasing exposures of ethanol. (B) A plot of the friction at a specific load (10 nN) versus ethanol exposure illustrates the significant reduction in friction that occurs at  $\sim 1$  ML coverage of a surface reaction layer. Both the existence of a reaction layer and its coverage were established through correlated measurements with additional techniques described in the text.

### 3.2. Temperature programmed desorption

The results of the thermal desorption measurements of several coverages of ethanol on VC are shown in Fig. 2. These experiments, described in greater detail elsewhere in conjunction with the reactivity of other short chain alcohols [14], demonstrate the stability of ethanol and its reaction products as a function of surface temperature. In

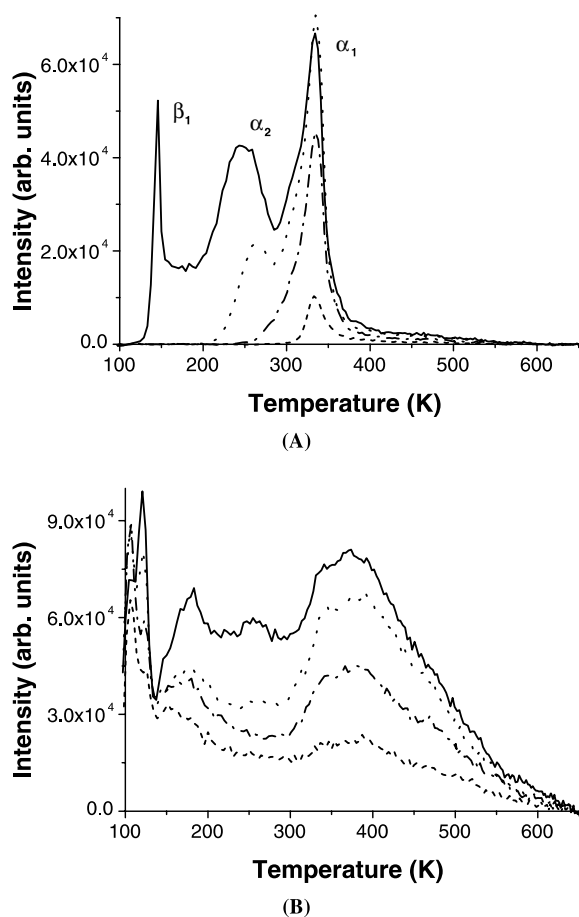


Fig. 2. (A) The desorption spectrum for the most abundant cracking fragment of molecular ethanol ( $m/q = 31$ ). TPD data were collected after exposing clean VC(100) at 100 K to various quantities of ethanol. The data show that, as coverage is increased, ethanol forms 2 ML states ( $\alpha_1, \alpha_2$ ) before finally forming a multilayer ( $\beta$ ). (B) The desorption spectra of ethene ( $m/q = 28$ ) produced through the decomposition of the surface ethoxy species.

Fig. 2A, the  $m/q$  31 signal represents the desorption of molecular ethanol from the surface while the  $m/q$  28 data of Fig. 2B represent the desorption of ethene as a reaction product. The molecular desorption state of ethanol centered at 335 K (Fig. 2A) arises from the recombination of a surface ethoxy and surface hydrogen species, and possesses intensity extending below room temperature. From these data, it is apparent that the room temperature conditions employed for the

tribological experiments described above represent a point where only intermediate species related to the desorption of ethene will be present. Specifically the data imply that the surface hydrogen and ethoxy species leading to molecular ethanol desorption will not be stable during the room temperature exposure or measurements of the tribological properties. In contrast, the desorption of the ethene reaction product (Fig. 2B) begins at low temperatures and extends to 600 K. We note that it is difficult to interpret the exact shape of the ethene desorption traces at 300 K due to the high background at low temperature; however, we find that the breadth and high temperature of the desorption feature suggest the surface species giving rise to ethene production remains on the surface to some extent at room temperature. The nature of this surface intermediate has been more fully characterized through analogous HREELS measurements described below.

### 3.3. High resolution electron energy loss spectroscopy

Fig. 3 displays the HREELS spectra of the VC(100) surface under three separate conditions: (A) clean, (B) following a 2.5 L exposure of ethanol at 150 K, and (C) the same surface annealed to 323 K. Again, these data are recorded elsewhere in greater detail with the complete assignment of the vibrational spectrum [10]. Briefly, the single loss feature at  $500 \text{ cm}^{-1}$  of the clean spectrum arises from the V–C stretch of the surface atoms, the additional vibrational features of spectrum B are characteristic of a surface ethoxy species, and the features of spectrum C are assigned to a surface intermediate involving the dehydrogenation of the surface ethoxy that occurs with increasing surface temperature. For the purposes of this publication, specific attention is drawn to the change in the vibrational spectra that occurs upon warming the surface dosed at 150 K to above room temperature. Most notably, the  $876$  and  $1050 \text{ cm}^{-1}$  peaks assigned to the strongly coupled  $\nu(\text{C–C})$  and  $\nu(\text{C–O})$  vibrations of the surface ethoxy species are replaced with the features at  $904$  and  $1120 \text{ cm}^{-1}$ . Spectra collected as a function of a more finely spaced temperature increments have isolated this

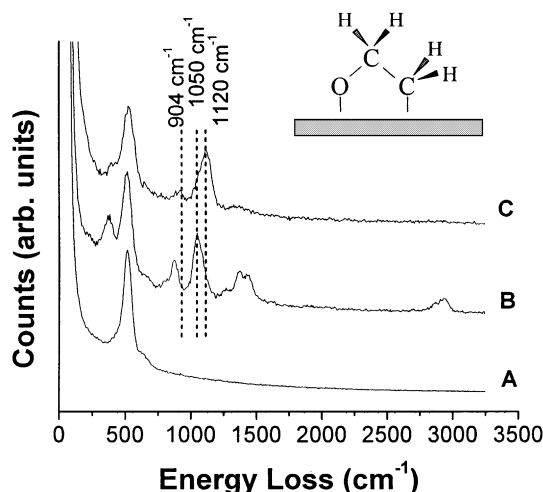


Fig. 3. The HREELS spectra of (A) clean VC(100), (B) 2.5 L exposure of ethanol to the VC surface held at 150 K, and (C) the ethanol-exposed surface annealed to 323 K. The dramatic change in the vibrational spectra between 150 and 323 K indicates a change in the molecular nature of the adsorbed surface species as well as the presence of the species at room temperature.

change to the range of 275–300 K (data not shown). We have assigned these vibrational features to a surface species bonded through both oxygen and carbon of the ethanol adsorbate, in analogy to the dioxymethylene species detected by Dilara et al. upon the reaction of methanol with  $\text{ZrO}_2(110)$  [15]. Data presented elsewhere suggest that the intermediate species formed on VC involves a bond between oxygen and vanadium [16]. The exact nature of the carbon-surface bond is not known at this time. It is this surface intermediate that gives rise to ethene desorption between 300 and 600 K and the changes observed in the tribological properties with increasing exposures of ethanol.

### 3.4. Photoelectron spectroscopy

Two additional spectroscopies have been employed to characterize the results of exposing ethanol to the VC(100) surface at room temperature, conditions identical to those encountered in the tribological measurements. First, XPS was used to follow the uptake of ethanol as a function of ex-

posure. Integrated intensities of the C 1s and O 1s signals were measured following a number of exposures of ethanol. These exposures were performed in a sequential fashion without cleaning the substrate between doses. The analysis of these data excluded intensity arising from the carbide carbon of the surface and a small amount of residual oxygen present on the surface before dosing. The results of the integrated C 1s and O 1s intensities, normalized by sensitivity factors, are shown in Fig. 4A and clearly indicate the formation and growth of an interfacial reaction layer with increasing ethanol exposures. Consistent with the significant change in interfacial friction observed for exposures greater than 1000 L, a change in the composition of the reaction layer is noted above these exposures. This is more clearly seen by plotting the ratio of integrated intensity, corrected for sensitivity factors, of the C 1s to O 1s regions as a function of ethanol exposure. Below 1000 L, the resulting surface species possess a stoichiometry of approximately two carbons to one oxygen. This composition is consistent with the picture generated from the low coverage HREELS data that portrayed a partially dehydrated surface ethoxy species bonded to the surface through both the carbon and oxygen [14]. (HREELS experiments were attempted following analogous large room temperature exposures of ethanol, however were not successful due to a dramatic loss in signal presumably due to changes in the work function of the spectrometer). Above 1000 L, the reaction layer is observed to continue to grow, however the film becomes carbon rich. The exact molecular nature of this species or the reaction pathway of its formation is not evident from these data; however, it likely can be described as an amorphous network of hydrocarbon species formed through the reaction of the surface film and gas phase ethanol.

Second, UPS measurements were performed in an analogous fashion, however fewer coverages were investigated. The data from these measurements are shown in Fig. 5. In Fig. 5A, the raw valence band spectra of the VC(100) surface are displayed when clean, and following ethanol exposures of 500, 1000, 1500, 2500 L. In the clean spectrum (uppermost trace), several features characterize the VC surface. These features result from

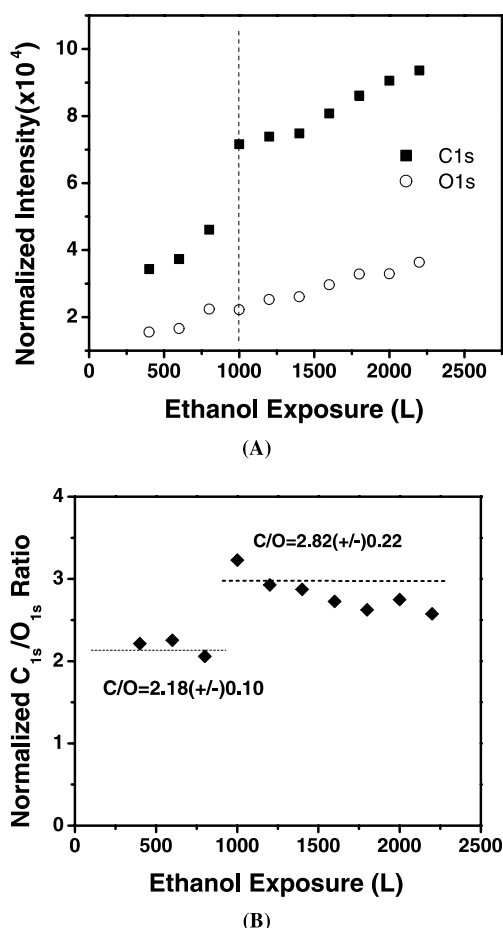


Fig. 4. (A) Integrated XPS C 1s (noncarbide) and O 1s intensities were measured as a function of increasing exposure of ethanol to the VC surface held at room temperature. (B) A plot of the ratio of the C 1s to O 1s integrated intensities illustrates the compositional difference between the exposures below and above 1000 L. The dotted lines represent the average of the ratios in different regimes. Below 1000 L, the C/O ratio is consistent with the composition of the species identified through the HREELS measurements. Above 1000 L, exposures of ethanol produce a carbon rich reaction layer.

the ionization of valence orbitals that have a predominant atomic orbital character. The peak located at 0.4 eV arises from a partially filled V 3d orbital, the peak at 3.5 eV arises from the C 2p orbitals, and the peak located at approximately 11 eV is associated with the C 2s orbitals. The peak at 5.5 eV is known to have contributions arising from both C 2p orbitals and from a small oxygen con-

taminant on the surface that could not be removed through our cleaning procedures. Dosing the VC surface with increasing exposures of ethanol at room temperature clearly produces a number of changes in the spectrum as seen in the lower traces of Fig. 5A. These changes are evident in the difference spectra calculated from the clean and dosed spectra. This procedure has involved the normalization of the dosed spectra to account for the attenuation of the VC features with increasing coverage of the reaction layer. The spectra of Fig. 5B contain three additional peaks at 4.5, 8, and 14 eV characteristic of the reaction layer species. The spectral intensities are consistent with a growing coverage of the reaction layer with increasing exposure. We have not attempted to assign these features in a molecular sense in light of the complex nature of the surface intermediate. However, we do note that the difference spectrum between the 1500 and 2500 L spectra contains only the 4.5 and 8 eV peaks in different proportions. This result is consistent with a change in the chemical nature of the adsorbate, which is also reflected in the change in surface composition observed with XPS above 1000 L.

### 3.5. Surface morphology

Finally, the room temperature interaction of ethanol with the VC(100) surface has been investigated with STM and AFM. In these measurements, spatially resolved changes in the morphology of the VC surface have been observed as a function of ethanol exposure. The results of the measurements performed with STM are summarized in Fig. 6. This figure includes  $500 \times 500 \text{ \AA}^2$  fixed current images of (A) the clean VC surface, and the surface following ethanol exposures in the amount of (B) 500 L, (C) 1500 L, and (D) 4000 L. It is important to note these images have not been collected in the identical region of the surface and therefore individual features cannot be compared between the images. Instead, a careful analysis of the surface structure reveals an unexpected growth mechanism for the reaction layer. In the displayed image of the clean surface, and in others collected in neighboring areas, steps separate terraces approximately 50–200 Å in width. The steps

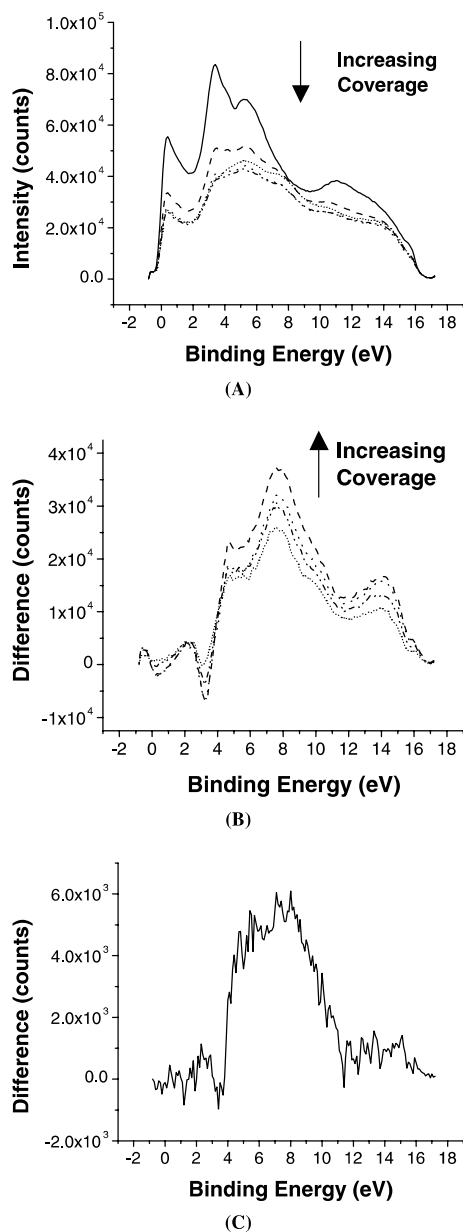


Fig. 5. (A) The valence band spectra measured by UPS for the clean VC(100) surface (upper trace) and for sequential room temperature exposures of ethanol totaling 500, 1000, 1500, and 2500 L. (B) The difference spectra between the clean and ethanol-exposed surface illustrate the formation of a reaction layer and the relatively small perturbation of the electronic structure of the underlying VC substrate. (C) Subtraction of the 1500 L data from the 2500 L data illustrates the compositional difference between the species formed in the first layer and those for higher coverages.

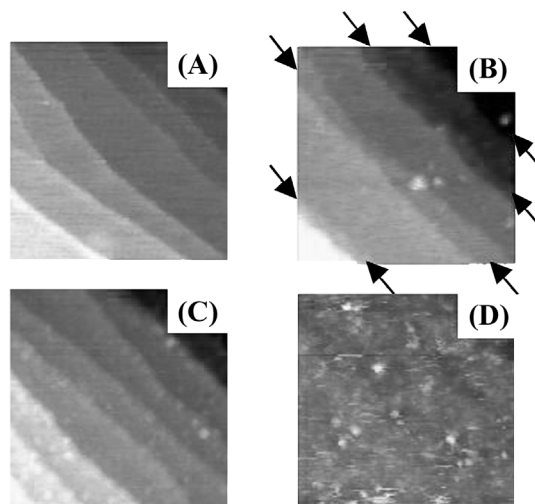


Fig. 6. STM images of scan area  $500 \times 500 \text{ \AA}^2$  were acquired of the clean VC surface and following 500, 1000, and 4000 L room temperature exposures of ethanol. (A) On clean VC(100), step heights correspond to fraction or multiples of the VC unit cell dimension and separate terraces 50–200 Å in width. (B) Following a 500 L ethanol exposure, new terraces 20–40 Å in width and  $\sim 1.2 \text{ \AA}$  in height appear along the lower terraces of the step edges (indicated by arrows). (C) Following a 1500 L exposure, the surface is conformally covered with the reaction layer while (D) 4000 L exposures generate a thicker amorphous reaction layer film effectively filling in the step structure.

are characterized as having heights of 0.5, 1, or 1.5 times the unit cell dimension of VC (4.16 Å). Upon careful inspection of the 500 L image, a second class of terrace structure is observed with step edges running roughly parallel to the substrate steps. This is displayed more clearly in Fig. 7A that contains a 3D plot of the region containing one of the new terrace structures (indicated by arrows). We attribute this terrace structure to the reaction layer by analyzing the step height. Fig. 7B displays the average of 15 individual line traces taken across the region of the newly formed terrace. The data have been offset to highlight the step height of the largest step corresponding to the unit cell dimension and the step height ( $\sim 1.2 \text{ \AA}$ ) of the reaction layer. Referring again to Fig. 6, following exposure of 1500 L of ethanol, the more narrow terraces are no longer observable and features 2–8 Å in apparent height begin to form across the surface (bright spots in images 6B–D). An analysis of the image of Fig. 6C and others in



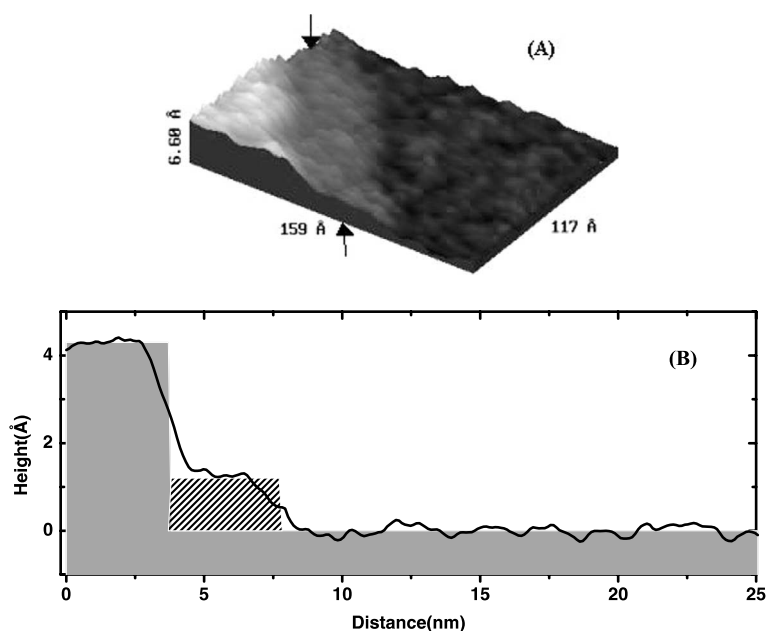


Fig. 7. (A) A magnified 3D view of the 500 L image of Fig. 6B illustrates the initial stages of reaction layer formation. (B) A line profile averaged over 15 cross-sectional plots along the steps reveals the apparent step heights of the substrate ( $\sim 4$  Å) and the reaction layer ( $\sim 1.2$  Å).

surrounding areas finds again step heights corresponding to only multiples of unit cell dimensions. This observation indicates that by 1500 L exposure, the reaction layer has covered the VC surface and additional growth has begun to occur. At the highest exposures investigated in this study (4000 L, Fig. 6D), it is difficult to resolve any step structure, and thus portrays the formation of an amorphous reaction layer.

The formation of a complete surface reaction layer that influences the tribological character of the VC surface is supported by similar AFM measurements. Fig. 8 displays  $2500 \times 2500 \text{ Å}^2$  images of the VC surface collected before (upper) and after (lower) exposure to 1500 L of ethanol. Images A and C represent the topography of the surface measured through the detection of the normal force acting on the AFM cantilever as a function of its location across the surface. Images B and D represent the frictional response of the surface measured through the simultaneous detection of the lateral force. Albeit lower resolution than the STM images of Fig. 6, topographic AFM

images of the clean surface clearly depict a surface comprised of steps and terraces. The frictional image of the surface illustrates a spatial inhomogeneity of the interfacial friction, with higher friction correlating to the position of step edges. Upon exposure to 1500 L of ethanol, the terrace structure is much less evident in the topographic image and the frictional image is largely featureless. The average friction measured over the entire frictional images, collected at 0 nN applied load, are 9.8 and 5.1 nN for the clean and ethanol-exposed surface with rms deviations of 1.7 and 0.75 nN respectively. The magnitude of friction reduction as well as the decrease in deviation is consistent with the friction-load measurements presented in Fig. 1.

#### 4. Discussion

Together, the data presented in the previous section portray a complete picture of the modification of the tribological properties of VC through

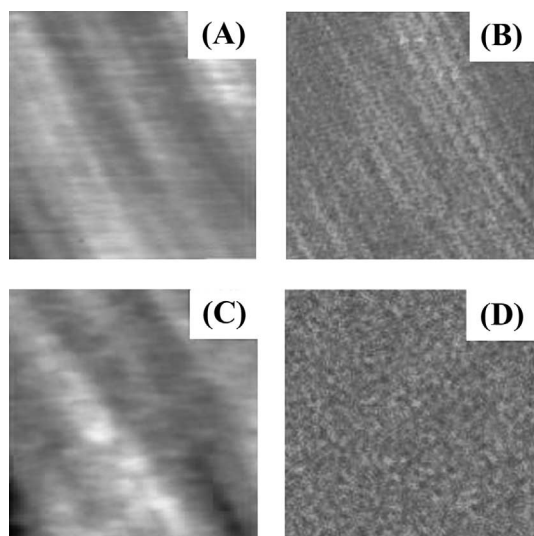


Fig. 8.  $2500 \times 2500 \text{ \AA}^2$  topography (left) and friction (right) images collected with AFM under UHV conditions for the clean VC(100) substrate (upper) and following a 1500 L room temperature exposure of ethanol (lower). The average of the frictional force, measured while sliding under a load of 0 nN applied load, decreases from a value of 7.2 nN on the clean surface to 3.8 nN following the 1500 L exposure of ethanol. Note also the reduction in resolution of the step edge structure in the friction images following the formation of the reaction layer film.

the adsorption of ethanol. Specifically, this picture entails the room temperature adsorption, albeit with a low sticking probability, and reaction of ethanol to form a stable surface species. Surface studies of the cryogenic dosing of ethanol and subsequent warming of the surface indicate that an ethoxy species is formed upon adsorption and is unstable at room temperature. This ethoxy intermediate reacts, either recombining with surface hydrogen to form gas phase ethanol or undergoes dehydrogenation producing a species bonded to the carbide surface through both oxygen and carbon of the molecule. Furthermore, the high exposures required to produce the hydrocarbon film and the alkene TPD profiles indicate that desorption of the dehydrogenated product in the form of ethene is also possible. However, at high enough exposures the surface reaction producing the chelated intermediate can be induced and it is the formation of this bonded species that leads to the

modification of the tribological properties. Although both friction and adhesion are observed to decrease with increasing exposures of ethanol, the friction undergoes a dramatic reduction, which is not observed for adhesion, at coverages near 1 ML. (The coverage leading to the formation of a complete monolayer has been roughly deduced from STM measurements.) As a result, we conclude that the reduction in friction does not arise simply from a reduction in interfacial adhesion between the  $\text{Si}_3\text{N}_4$  probe tip and the VC surface. We note that the data sets of Fig. 1A would be significantly offset at the lowest loads if the reduction in adhesion were the dominant mechanism leading to the reduction in friction. Instead, the data presented above support the picture of a friction reduction mechanism involving the formation of a stable reaction layer film exhibiting an inherently lower interfacial shear strength. The change in shear strength ( $S$ ) of the interface can be estimated from the interfacial area of contact ( $A_c$ ) and the measured interfacial friction ( $F_f$ ) ( $S = F_f/A_c$ ). Using tabulated values of the Poisson's ratio and Young's modulus of  $\text{Si}_3\text{N}_4$  [17], a similar carbide material [18], and values typical of bulk polymers [19,20], the interfacial contact area is estimated with a JKR model to be  $\sim 200 \text{ nm}^2$  with the reaction film and  $\sim 20 \text{ nm}^2$  with the clean carbide surface. (We note that these values have been calculated for comparison purposes only as it is difficult to fully assess quantitative areas due to differences in the contact mechanics of the two dissimilar materials.) From these values, we estimate an interfacial shear strength of 20 MPa at 10 nN applied load on the complete reaction layer and 450 MPa at 10 nN on the clean carbide surface. This change in interfacial shear strength is manifest in a reduction in the slope of the friction–load plots measured after ethanol exposures.

The results presented here contrast those of a number of other UHV studies of interfacial friction. For example, the formation of thin oxides (up to 25 Å) at iron surfaces cleaned in UHV has been observed to produce marked reductions in the friction of an iron pin sliding on an iron flat, even when significant wear of the interface occurred [21]. The reduction in friction has been interpreted in terms of the passivation of metal–

metal contact and bond formation (adhesion). While adhesion undoubtedly contributes to the interaction of the  $\text{Si}_3\text{N}_4$  tip with VC surface, we do not believe that the shearing of interfacial bonds is responsible for the friction measured on the clean surface. As a result, the formation of the hydrocarbon reaction film represents an alternative pathway to reduced friction.

Gellman and coworkers have measured the interfacial friction of clean single crystal metals as a function of exposure to a number of adsorbates [22–24]. In general, atomic adsorbates such as sulfur and chlorine produced a reduction in the static friction between two copper surfaces on the order of 30–40%, although the overall magnitude of friction remained high. In other work by Gellman, the friction of the  $\text{Cu}(111)$ – $\text{Cu}(111)$  surface was measured as a function of the uptake of trifluoroethanol. While the general form of the data presented in Fig. 1 bears some resemblance to their data, in terms of both the dramatic reduction in friction at a 1 ML coverage and the reduction in the standard deviation of the frictional values, a different mechanism is clearly operative. Most

significantly, trifluoroethanol exists as a physisorbed species on  $\text{Cu}(111)$  at the temperature of the friction measurements (120 K). Under these conditions, the reduction in friction, which undergoes a second reduction upon the completion of a second monolayer, was again interpreted in terms of the passivation of metal–metal contacts. They ascribe the lack of complete passivation at 1 ML to the mobility of the molecular adsorbate. In contrast, the data presented above clearly depict a strongly bound surface species formed on the VC surface upon exposure to ethanol. In this case however, the reduction in friction is not observed at incomplete coverages due to the spatial distribution of the reaction layer. While the origin of this particular growth mechanism is not fully understood, the STM and AFM data indicate that a significant reduction is not observed until the reaction layer “covers” the steps of the VC surface. This mechanism is schematically represented in Fig. 9. Together, the results of the present frictional study performed on a molecular scale uniquely highlight the contribution of local structure (atomic scale steps) to interfacial friction.

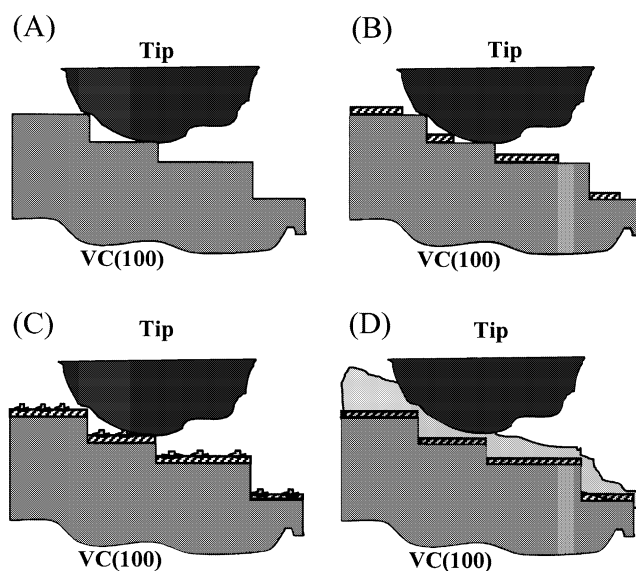


Fig. 9. From the collective data described in this report, a schematic model of the formation of the boundary layer film produced by the room temperature reaction of ethanol with the VC(100) surface has been developed. This picture portrays the interaction of a single asperity with the (A) clean VC surface and the subsequent modifications of the tribological interaction following (B)  $\sim 500$  L, (C)  $\sim 1500$  L, and (D)  $\sim 4000$  L exposures of ethanol. At exposures greater than  $\sim 1000$  L, a significant reduction in friction is observed and correlates with the formation of the first monolayer of the boundary layer film.

Finally, the results presented for the reduction in friction upon the adsorption of ethanol differ from those of our previous report of the influence of oxygen adsorption on VC [9]. In that work, a 100 L exposure of oxygen was observed to produce a stable surface vanadyl species ( $V=O$ ) and an  $\sim 40\%$  reduction in interfacial friction. While this study was not performed as a function of oxygen exposure, no change in interfacial adhesion was observed for this exposure that approached saturation coverage. Instead, the reduction in friction was interpreted in terms of a change in the interfacial electronic structure, namely a reduction in the electron density at the Fermi edge of the VC substrate. Although slight changes in the intensity of the valence band structure of VC were observed in the UPS data (Fig. 5), no substantial or coverage-dependent changes near the Fermi edge were detected.

The significance of the reduction in friction at the VC(100) surface with exposures to molecular ethanol is accentuated when considering the concept of vapor phase lubrication. This approach calls for the gas phase delivery of a lubricant species, and the subsequent formation of a stable, low friction, boundary layer. Although the exposures cited in this report are relatively large for UHV studies, they are actually quite small by atmospheric standards and the continual formation of an interfacial boundary layer could be expected even with small partial pressures of ethanol within the tribological system. While the saturation point of the reaction layer growth has not been identified, the XPS and STM studies clearly indicate the formation of a multilayer structure serving as a boundary layer lubricant of the tip–surface interaction. Future studies in our laboratory will explore the resilience of the ethanol reaction layer to interfacial wear and estimate the degree of friction reduction under macroscopic sliding conditions.

## 5. Conclusions

The frictional properties of the VC(100) surface have been measured with AFM as a function of the uptake and reaction of ethanol under UHV conditions. The reaction of ethanol with this sur-

face has been characterized with an array of surface analytical measurements, which provide a clear picture of chemical nature of the reaction layer formed under these conditions. Together, these measurements indicate that ethanol decomposes on the VC(100) surface at room temperature to eventually produce a carbon rich film which acts as a boundary layer separating the probe tip from the carbide surface, thereby lowering friction. The reduction of friction is attributed to the chemical modification of the carbide surface through the formation of a molecularly thin polymeric film possessing an inherently lower interfacial shear strength. These measurements also portray a novel growth pattern of the reaction film and the coverage dependent tribological properties of this boundary layer film.

## Acknowledgements

This work has been supported by the AFOSR under contract 49620-00-1-0114 and by the NSF under a Career Award to SSP (CMS 9876042). Partial support has also been provided through The Aerospace Corporation IR&D program funded by the Space and Missile Systems Center (SMC) of the USAF under contract number F04701-00-C-0009. The authors wish to thank Paul Adams of The Aerospace Corporation for his assistance in sample preparation.

## References

- [1] M.P. Delplancke, V. Vassileris, R. Winand, *J. Vac. Sci. Tech.* 1393 (1995) 1104.
- [2] O.R. Monteiro, M.P. Delplancke-Ogletree, I.G. Brown, *Thin Solid Films* 342 (1999) 100.
- [3] O.R. Monteiro, M.P. Delplancke-Ogletree, R.Y. Lo, R. Winand, I.G. Brown, *Surf. Coatings Tech.* 94–95 (1997) 220.
- [4] H. Berndt, A.-Q. Zeng, H.-R. Stock, P. Mayr, *J. Physique IV* 3 (C3) (1993) 313.
- [5] W.J. Sessler, M.S. Donley, J.S. Zabinski, S.D. Walck, V.J. Dyhouse, *Surf. Coatings Tech.* 56 (1993) 125.
- [6] J. Vetter, R. Rochotzki, *Thin Solid Films* 192 (1990) 253.
- [7] R.F. Bunshah (Ed.), *Handbook of Hard Coatings*, Noyce Publications, Park Ridge, New Jersey, 2001.

- [8] S. Lee, O. El-bjeirami, S.S. Perry, S.V. Didziulis, P. Frantz, G. Radhakrishnan, *J. Vac. Sci. Tech.* 18 (2000) 69.
- [9] P.B. Merrill, S.S. Perry, *Surf. Sci.* 418 (1998) 342.
- [10] R.L. Guenard, L.C. Fernandez-Torres, B.-I. Kim, S.S. Perry, P. Frantz, S.V. Didziulis, *J. Phys. Chem.* 2000, submitted for publication.
- [11] S.S. Perry, P.B. Merrill, *Surf. Sci.* 383 (1997) 4938.
- [12] D.F. Ogletree, R.W. Carpick, M. Salmeron, *Rev. Sci. Instrum.* 67 (1996) 3298.
- [13] P.B. Merrill, S.S. Perry, P. Frantz, S.V. Didziulis, *J. Phys. Chem.* 102 (1998) 7606.
- [14] S.V. Didziulis, P. Frantz, L. Fernandez, R. Guenard, O. El-bjeirami, S.S. Perry, *J. Phys. Chem. B* (2001), in press.
- [15] P.A. Dilara, J.M. Vohs, *Surf. Sci.* 321 (1994) 8.
- [16] P. Frantz, S.V. Didziulis, *Surf. Sci.* 412/413 (1998) 384.
- [17] M.A. Lantz, S.J. O'Shea, A.C.F. Hoole, M.E. Welland, *Appl. Phys. Lett.* 70 (1997) 970.
- [18] L.E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1991.
- [19] L.E. Nielson, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1975.
- [20] T.P. Weihs, Z. Nawaz, S.P. Jarvis, J.B. Pethica, *Appl. Phys. Lett.* 59 (1991) 3536.
- [21] B.M. DeKoven, P.L. Hagans, *J. Vac. Sci. Tech. A* 8 (1990) 2393.
- [22] C.F. McFadden, A.J. Gellman, *Surf. Sci.* 409 (1998) 171.
- [23] C.F. McFadden, A.J. Gellman, *Langmuir* 11 (1995) 273.
- [24] C.F. McFadden, A.J. Gellman, *Trib. Lett.* 1 (1995) 201.