Activation of the SiC surface for vapor phase lubrication by Fe chemical vapor deposition from $Fe(CO)_5$

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Received 31 July 2000; accepted 20 October 2000

The feasibility is demonstrated of a new approach to the vapor phase lubrication of ceramics using organophosphorus compounds. The surface of SiC is shown to be unreactive for the decomposition of trimethylphosphite, $(CH_3O)_3P$, a simple model for organophosphorus vapor phase lubricants such as tricresylphosphate. In order to activate the surface of SiC it has been exposed to $Fe(CO)_5$ at a temperature of 600 K. Chemical vapor deposition serves as a means of depositing Fe on the SiC surface. The Fe-modified SiC surface is then shown to induce the decomposition of adsorbed $(CH_3O)_3P$. The mechanism of $(CH_3O)_3P$ decomposition is similar to that observed on Fe(110) surfaces modified by the presence of oxygen. It is initiated by P–O bond cleavage to produce adsorbed methoxy groups, $CH_3O_{(ad)}$, which then decompose by β-hydride elimination resulting in H_2, CO, H_2CO, and CH_3OH desorption. It is suggested that chemical vapor deposition of metals using high vapor pressure metal-containing compounds such as $Fe(CO)_5$ can serve as a mechanism for continuous, *in situ* activation of ceramic surfaces for vapor phase lubrication in high temperature engines.

KEY WORDS: lubrication; vapor phase lubrication; SiC; Fe deposition

1. Introduction

The lubrication of ceramic surfaces working at extremely high temperatures has been the focus of a number of recent tribological studies [1–10]. The high physical strength, low density, and chemical stability of ceramic materials such as SiC and Si_3N_4 make them ideal for use in high-speed turbine engines and high temperature, low heat rejection engines that are expected to work at temperatures above 500 °C [2,3,11,12]. Since liquid lubricants cannot withstand such extreme conditions, a number of non-liquid lubrication systems such as vapor phase lubrication (VPL), solid powder lubricants, and catalytic carbon deposition have been explored as alternatives for high temperature applications [1–19].

VPL has received a great deal of attention over the past decade as an approach for the lubrication of high temperature engines. In VPL, lubricants are delivered to contacting surfaces in vapor form. The vaporized lubricants react at the hot surfaces of working engine parts to form tribopolymers that reduce wear [2]. A variety of lubricants have been tested with metals, alloys and ceramics and have shown excellent anti-wear properties at temperatures ranging from 300 to 800 °C [1–15]. Of these VP lubricants, phosphorus-containing organic compounds such as tricresylphosphate (TCP), *t*-butylphenylphosphate, and cyclophosphazene have been the most widely used. At high temperatures these compounds are thought to react with iron-containing surfaces to form thin films of polyphosphate glasses containing carbon [15]. It is these thin films that provide lubrication and reduce wear. Recently, the development of VPL technology has advanced to the stage of being demonstrated for practical applications [20].

Although the organophosphorus VPL compounds work well with iron and iron-based materials, difficulties arise when VPL technology is applied to ceramic materials or some high temperature alloys. Early studies showed that TCP, the most commonly used vapor phase lubricant, generates flaky deposits on surfaces of inert materials such as SiC, Si_3N_4 and quartz [8,9]. Tribological tests showed that the flaky deposits provide no anti-wear protection [8]. In order to overcome this problem, techniques were developed to treat the ceramic or alloy surfaces with iron coatings prior to VPL tests. These Fe deposition methods included chemical deposition and electrodeposition [2,4,5,12]. Although these Fe coatings can activate the ceramic surfaces and consequently reduce wear during VPL tests, a general problem associated with these static coating techniques is that the Fe coatings cannot be replenished *in situ*. Once these Fe coatings have worn through, severe wear of the ceramic substrates occurs. As a result, periodic treatment of the surfaces would be necessary if ceramic engine parts were expected to work for prolonged periods using VPL. Alternatively, it has been found that metallic surface films on ceramics can be generated through sliding contact with metal surfaces [1,3]. At metal–ceramic interfaces, metal residue was detected on the ceramic surfaces. While this could aid VPL by activating the ceramic surface this approach evidently cannot be applied to all-ceramic systems. What is needed for continuous VPL of all-ceramic engines is a method for continuous *in situ* activation of ceramic surfaces during engine operation.

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1023-8883/01/0400-0179$19.50/0

This study proposes a new method to activate ceramic surfaces that can, in principle, be used for continuous deposition of Fe onto ceramic surfaces in an operating engine. Volatile metal-containing compounds, such as $Fe(CO)_5$, can be exposed to ceramic surfaces in vapor form to deposit Fe films that activate the ceramic surfaces for VPL. This vapor phase delivery technique or chemical vapor deposition (CVD) has two distinct advantages over previous static activation methods. First, the active metal layers can be continuously deposited onto the ceramic surfaces during engine operation. Secondly, the deposition rate of the thin metal films can be controlled in real time, and selected lubricants can be delivered to ceramic contact areas based on operating conditions and needs in order to achieve optimal lubrication.

A metal vapor delivery mechanism has probably been observed serendipitously in previous work by Graham et al., in which Cu was found on ceramic surfaces after tribological tests [3]. It was suggested that the Cu had been transferred to the ceramic surfaces by unknown vapor phase compounds produced from a reaction of TCP with the copper tubing used to deliver the TCP vapor. A later study used a copper coil to react with TCP vapor in order to transfer activating deposits to a ceramic test plate [2]. Friction measurements on the ceramic plate showed an initial reduction of the friction coefficient, but high friction after the copper coil was covered with polymer generated by the reaction with TCP and ceased depositing metal onto the ceramic surface.

In order to demonstrate the feasibility of the vapor phase metal delivery in this investigation, volatile iron pentacarbonyl, $Fe(CO)_5$, was delivered to a SiC surface to form an Fe film that activated the SiC surface for reaction with a model organophosphorus compound, trimethylphosphite, $(CH_3O)_3P$. $Fe(CO)_5$ was chosen for these experiments for a number of reasons. First, $Fe(CO)_5$ has reasonably high vapor pressure at room temperature and can been easily introduced into the ultrahigh vacuum (UHV) chamber used for these studies. Secondly, the decomposition mechanism of $Fe(CO)_5$ on single crystal Si and some metal surfaces has been studied quite extensively [21–24]. It is known that $Fe(CO)_5$ undergoes thermal decomposition to deposit Fe onto Si surfaces at temperatures above 500 K. Thirdly, the decomposition mechanism of $(CH_3O)_3P$, our model VP lubricant, has been studied on the clean Fe(110) surface and thus there is a basis for understanding its chemistry on the thin Fe films that we produce from $Fe(CO)_5$ on SiC surfaces [25]. Finally, tribological studies have demonstrated that Fe coatings generated by static methods can activate ceramic surfaces for VPL [2,4–6]. If CVD methods can be used to deposit Fe onto SiC then they are expected to have the same tribological properties as surfaces activated by deposition of Fe films using other methods.

The choice of SiC as a ceramic substrate for VPL experiments was based on the fact that polycrystalline SiC is a widely used engineering material and single crystalline SiC is readily available for our studies. The processing of SiC surfaces is itself of great importance in the development of semiconductor devices and thus there is ample discussion in the literature of methods for preparing reproducible SiC surfaces [26–32]. At the time of writing this article, however, there appear to be no reports of methods for metallization of SiC surfaces by CVD using $Fe(CO)_5$ or any other such compounds.

The organophosphorus compound chosen as a model VP lubricant for this work has been $(CH_3O)_3P$. This contains the P–O–C linkages that are present in TCP and there have been several recent studies of its surface chemistry on Fe(110) and other metal surfaces [25,33–35]. Those studies indicate that $(CH_3O)_3P$ decomposes by a mechanism that first produces methoxy intermediates, $CH_3O_{(ad)}$, that then decompose by β-hydride elimination to produce H_2, CO, formaldehyde (H_2CO), and methanol (CH_3OH). This previous work provides a foundation on which to base our understanding of $(CH_3O)_3P$ surface reactions with the Fe-modified SiC surfaces.

The results obtained in this study will show that Fe coatings can be readily formed on the SiC surface by exposure to $Fe(CO)_5$ at 600 K. On the unmodified SiC surface $(CH_3O)_3P$ adsorbs reversibly and during heating desorbs molecularly with little decomposition. In contrast, $(CH_3O)_3P$ reacts on the Fe-modified SiC surface to yield H_2, CO, H_2CO and CH_3OH desorption at 450 K. The ability to deposit Fe onto SiC by CVD and the fact that once deposited the Fe activates the SiC surface for reaction with $(CH_3O)_3P$ demonstrates the feasibility of activating ceramic surfaces with volatile metal-containing compounds and the potential for combining CVD with VPL for sustained lubrication of high temperature ceramic engines.

2. Experimental

The experiments described in this article were all performed in an UHV surface analysis chamber. The chamber is equipped with an Ar^+ ion sputter gun for surface cleaning, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a low-energy electron diffraction (LEED) optics for analysis of surface structure, and a quadrupole mass spectrometer for detection of desorbing species during temperature-programmed desorption (TPD) spectrometry. Three standard leak valves were used to introduce gaseous species into the UHV chamber for deposition or adsorption onto the SiC surface. The single crystal SiC sample was mounted to an UHV manipulator that allowed it to be moved within the chamber and to be heated and cooled through a temperature range of 180–1200 K.

The SiC sample was an n-doped (N, $(2\text{–}4) \times 10^{18}\ \mathrm{cm}^{-3}$) 6H-SiC single crystal obtained commercially from Cree Research, Inc. The Si-terminated (0001) surface was used for these experiments. The crystal was diced into a 10×10 mm square and clamped to a tantalum plate. A K-type thermocouple was attached to the back of the tantalum plate for temperature measurements. The plate was spot-welded to the sample holder on the UHV manipulator through two tantalum wires. The SiC crystal was initially cleaned according to a published procedure by HF chemical etching before introduction into the UHV chamber [30]. After bakeout of the UHV chamber, AES of the SiC surface revealed only Si, C, and a trace amount of O. A 1×1 LEED pattern was seen after annealing the crystal to temperatures in the range 500–1200 K.

Although the SiC sample was single crystalline we make no claim to have worked with the ordered SiC(0001) surface during the course of these experiments. Since the purpose of this work has been to emulate a process that might be expected to occur on the surface of a ceramic engine component this was not deemed to be necessary. The preparation of a clean and ordered stoichiometric SiC(0001) surface is quite an involved process and cannot be achieved by simple Ar^+ ion sputtering and annealing treatments [26–28]. This is due to the fact that the Si preferentially evaporates during the annealing needed to remove damage caused by Ar^+ sputtering, leaving a carbon rich surface. In order to create a stoichiometric surface, annealing must be performed in a flux of vapor phase Si atoms. Since we intended to perform experiments that involve the repeated deposition of Fe and P onto the surface we needed a straightforward method for removing these contaminants that does not require removal of the sample from the chamber and chemical etching. We have chosen to remove contaminants by low temperature (200 K) sputtering with 2000 eV Ar^+ ions. We did not perform any annealing of the sample following sputtering. This procedure generated a surface with a reproducible $Si_{90eV} : C_{272eV}$ AES peak-to-peak height ratio of 1.7 : 1. Using tabulated AES sensitivity factors we determine that the Si : C ratio of the surface is roughly 1 : 1.1 [36]. Thus the surface is close to stoichiometric but has no long range order. We believe such a surface is sufficient for the purposes of this investigation.

The Fe coating was deposited by exposing the SiC surface at elevated temperature, typically 600 K, to $Fe(CO)_5$ vapor at 2×10^{-8} Torr. After Fe deposition, the SiC sample was exposed to $(CH_3O)_3P$ for adsorption at 190 K. The exposure was high enough to saturate the Fe-modified SiC surface. The surface was then positioned in front of the aperture to the mass spectrometer and heated at 2 K/s for TPD studies.

The $(CH_3O)_3P$ was obtained from Aldrich Chemical Co. at a purity of 99+%. The $Fe(CO)_5$ was also obtained from Aldrich at a purity of 99+%. Both were further purified by freeze–pump–thaw cycles on the manifold of the UHV chamber before introduction into the UHV chamber. The $Fe(CO)_5$ sample vial was kept in a Dewar flask containing ice water when it was not in use but still attached to the UHV chamber.

3. Results and discussion

3.1. $(CH_3O)_3P$ on the SiC surface

Before modifying the SiC surface with Fe it was necessary to establish the baseline reactivity of $(CH_3O)_3P$ on the unmodified SiC surface. It is important to note that the SiC surface that we have worked with is not a truly ordered, clean, and stoichiometric SiC(0001) surface. It was produced by sputtering with 2000 eV Ar^+ ions at 200 K for periods of 60 min. Although this surface has a Si : C ratio of 1 : 1.1, a near stoichiometric SiC, it is undoubtedly highly defective and contains some residual oxygen that could not be removed by sputtering.

Ceramic surfaces such as those of SiC tend to be chemically inert and this is probably the root cause of their poor performance with VP lubricants such as TCP. The thermally programmed desorption (TPD) spectra of $(CH_3O)_3P$ adsorbed on the SiC surface are shown in figure 1 and reveal that it does not react significantly on SiC. The $(CH_3O)_3P$ was adsorbed on the SiC at 190 K using a dose that was sufficient to saturate the surface. The ionization fragments monitored during the TPD experiment were at $m/q = 2$ (H_2^+), 28 (CO^+), 29 (HCO^+), 31 (CH_3O^+), and 47 (PO^+). In the low temperature range from 200 to 380 K there is a broad desorption feature with a fragmentation pattern that indicates desorption of molecular $(CH_3O)_3P$. A small amount of decomposition is indicated by the desorption of H_2 and CO in the temperature range 400–500 K. As will be seen this

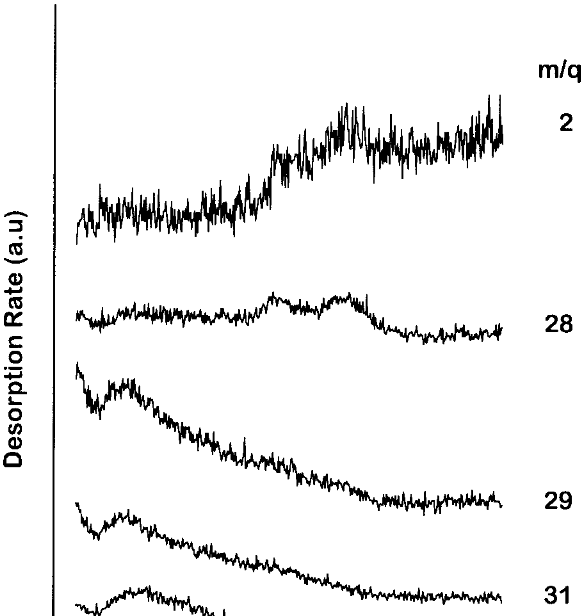

Figure 1. Temperature-programmed reaction spectra of adsorbed $(CH_3O)_3P$ on a SiC surface. The SiC single crystal was prepared by Ar^+ sputtering at 200 K. A saturated film of $(CH_3O)_3P$ was adsorbed at 190 K. The detection of ionization fragments with $m/q = 2$, 28, 29, and 47 indicates reversible desorption of adsorbed $(CH_3O)_3P$ in the temperature range 200–320 K. Fragments with $m/q = 2$ and 28 suggest trace amounts of $(CH_3O)_3P$ decomposition to produce H_2 and CO. These H_2 and CO are negligible when compared with those observed desorbing from the Fe-activated SiC surfaces. The heating rate was 2 K/s.

is substantially less than the amount that appears during decomposition of $(CH_3O)_3P$ on the Fe-modified SiC surface. Clearly the majority of the $(CH_3O)_3P$ is reversibly adsorbed and desorbs from the surface rather than reacting during heating.

Auger electron spectroscopy analysis also revealed that very little of the $(CH_3O)_3P$ decomposed on the SiC surface. A small amount of P appeared on the SiC surface after the $(CH_3O)_3P$ TPD experiment. In contrast, adsorption and heating of $(CH_3O)_3P$ on the Fe-modified surface will be shown to result in the deposition of substantial amounts of P. The P deposited on the clean SiC surface is less than 20% of that deposited on the Fe-modified SiC surface. The net results of the adsorption and TPD experiments using $(CH_3O)_3P$ on the unmodified SiC surface are consistent with expectations. There is very little reaction of the $(CH_3O)_3P$ on the SiC surface and the majority desorbs during heating.

3.2. $Fe(CO)_5$ deposition on SiC

The deposition of Fe onto the SiC surface during exposure to $Fe(CO)_5$ was monitored using Auger electron spectroscopy. Figure 2(A) shows the Auger spectrum of the clean SiC surface produced by Ar$^+$ ion sputtering at 200 K. The Si_{90eV} and C_{272eV} features have relative intensities of 1.7 : 1 indicating relative concentrations at the surface of 1 : 1.1 as estimated using published Auger elemental sensitivities [36]. The peak at 211 eV is due to Ar embedded in the surface after sputtering and there is a peak due to residual O at 510 eV.

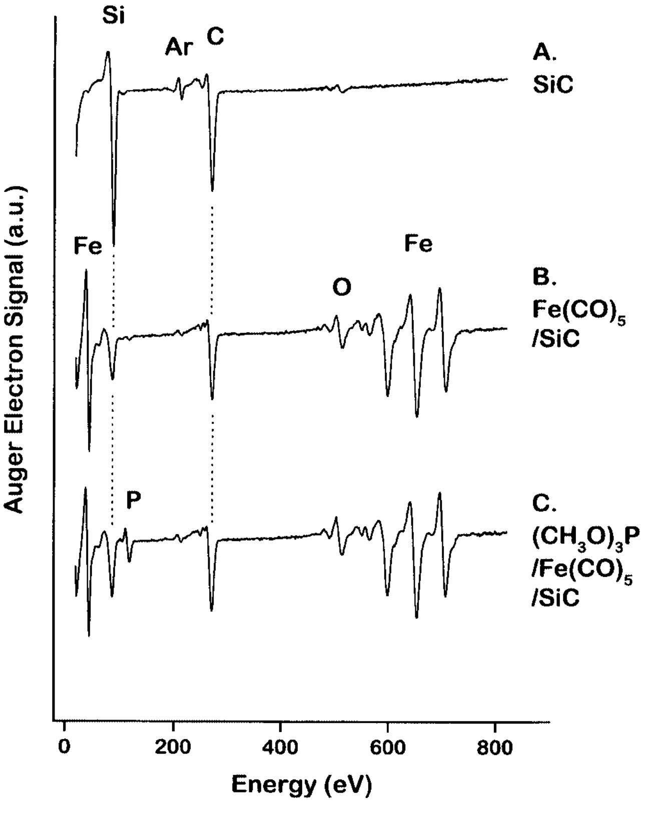

Figure 2. Auger spectra of SiC sample surfaces. (A) The clean SiC surface after Ar$^+$ sputtering. (B) The SiC surface after deposition of Fe by exposure to $Fe(CO)_5$ for 40 min at 2×10^{-8} Torr with the SiC surface at 600 K. The Fe : Si atomic ratio was about 3.3 : 1 as estimated from the Auger peak-to-peak intensity of Fe at 710 eV and Si at 90 eV and scaled by their Auger elemental intensities (0.21 for Fe and 0.35 for Si at 3 K primary beam voltage [36]). The relative intensity of the Si and C signals reversed in order from the clean SiC surface. (C) Fe-modified SiC surface after adsorption and thermal desorption of $(CH_3O)_3P$. P was left on the SiC surface.

Fe was deposited on the SiC surface by exposure to $Fe(CO)_5$ at a pressure of 2×10^{-8} Torr and a sample temperature of 600 K. Figure 2(B) shows an Auger spectrum of the surface after Fe deposition for a total of 40 min. There are a series of peaks in the energy range 600–700 eV and a single feature at 45 eV that are all characteristic of Fe. During exposure of the $Fe(CO)_5$ to the SiC surface the intensity of the Fe peaks increases roughly linearly with time. The AES sensitivity of Fe is 0.21, slightly greater than that of C, indicating that the coverage of Fe after 40 min is on the order of one monolayer. With respect to the Si signal, however, the Fe signal represents a coverage of roughly 3.3 monolayers. It is difficult to establish an absolute coverage scale for the Fe films at this point because the morphology of the layer is unknown and the degree to which it is screening the C signal cannot be determined. It is known that Fe films deposited on Si by $Fe(CO)_5$ vapor phase deposition grow by an island growth mechanism [21]. An island mechanism was also observed for physical vapor deposition of Ti on the SiC surface [31]. If this is the case for Fe deposition onto the SiC surface from $Fe(CO)_5$, then the Fe layer would be fully developed at much higher coverage than if deposited by a layer-by-layer deposition mechanism. There are many features of the surface chemistry of $Fe(CO)_5$ on SiC that remain unexplored at this point, however, it is quite clear from the data in figure 2 that this is a viable method for the deposition of Fe onto the SiC surface.

The deposition of Fe onto the SiC surface using $Fe(CO)_5$ causes some subtle changes in the Auger spectra of the surface. Comparison of figure 2 (A) and (B) reveals that the relative intensities of the Si and C peaks reversed in order. While the intensity of the C AES signal does not change much during Fe deposition the intensity of the Si signal drops substantially. There are several possible causes of this phenomenon. On the one hand, the screening of the Si signal at 90 eV by the Fe layer is likely to be more effective than the screening of the C signal at 272 eV [36,37]. It is also possible that the decomposition of $Fe(CO)_5$ results in the deposition of some C onto the surface. This has been observed during the deposition of Fe onto the Si surface from $Fe(CO)_5$ [22]. Finally, it is possible that the Fe causes the extraction of C from the SiC lattice to form an Fe carbide film at the surface.

3.3. $(CH_3O)_3P$ on Fe/SiC

In order to test the reactivity of the Fe-modified SiC surface towards organophosphorus compounds we have studied the chemistry of our model compound, $(CH_3O)_3P$, on this surface. The Fe-modified SiC surface shown in figure 2(B)

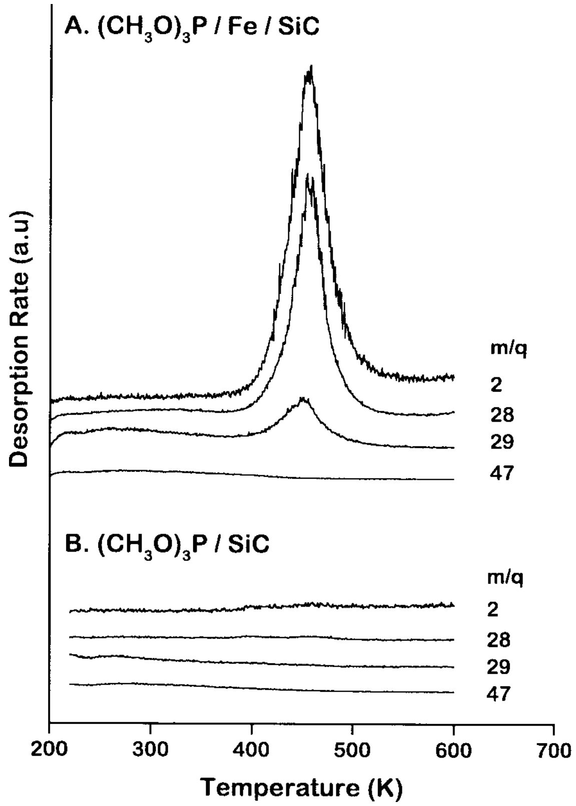

Figure 3. TPRS of $(CH_3O)_3P$ adsorbed on (A) the Fe-modified SiC surface and (B) the clean SiC surface. The SiC single crystal was prepared by Ar^+ sputtering at 200 K and Fe was then deposited by CVD using 2×10^{-8} Torr $Fe(CO)_5$ at 600 K for 40 min. A saturated film of $(CH_3O)_3P$ was adsorbed at 190 K and then heated at 2 K/s. Intense desorption features of species with ionization fragments at $m/q = 2$, 28 and 29 indicate decomposition of adsorbed $CH_3O_{(ad)}$ intermediates formed during the decomposition of $(CH_3O)_3P$. The spectrum of the fragment with $m/q = 47$ indicates that a small fraction of the adsorbed $(CH_3O)_3P$ desorbed as parent molecules in the temperature range from 200–320 K. The desorption spectra from the clean SiC surface are redrawn using the same scale in this figure for direct comparison with those from the Fe-modified surface.

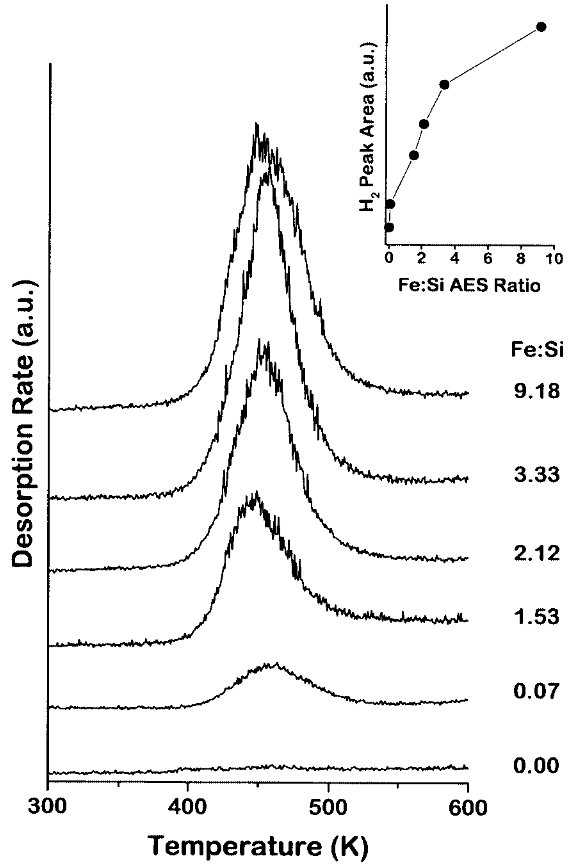

Figure 4. TPRS of hydrogen production from adsorbed $(CH_3O)_3P$ on Fe-modified SiC surfaces. The hydrogen desorption increases with the increase of Fe coverage. Fe was deposited by decomposition of $Fe(CO)_5$ on the SiC surface at 600 K. The Fe coverage is expressed in terms of the atomic Fe : Si ratio estimated using the relative Auger signal intensity. Saturation $(CH_3O)_3P$ adsorption was achieved by background dosing while the sample surface was kept at 190 K. The heating rate was 2 K/s. The inset shows the relative yields of hydrogen as the coverage of Fe is increased. At measured Fe : Si ratios above 4 : 1 the yield of hydrogen begins to plateau.

was exposed to a saturation exposure of $(CH_3O)_3P$ at 200 K. Figure 3 shows the TPD spectra obtained during heating at 2 K/s and compares the desorption to that observed from the clean SiC surface (as in figure 1). It is readily apparent from comparison of the spectra that the presence of the Fe film on the surface has a profound effect on the surface chemistry of the $(CH_3O)_3P$. At low temperatures there is still a broad desorption feature at $m/q = 47$ due to molecular $(CH_3O)_3P$. The primary differences between the desorption from the SiC and the Fe/SiC surfaces are in the $m/q = 2$, 28, and 29 desorption features at 450 K. These correspond to H_2^+, CO^+, and HCO^+, an ionization fragment of H_2CO. Additional spectra taken by monitoring fragments at $m/q = 30$, 31, and 32 indicate that the desorbing species include both H_2CO and CH_3OH with H_2CO as the major component. This distribution of products is very similar to that reported for $(CH_3O)_3P$ decomposition on the Fe(110) surface [25] and for methanol decomposition on the oxidized Fe(110) surface [38]. On the clean Fe(110) surface decomposition of $(CH_3O)_3P$ results in the desorption of CO and H_2 at 430 K. It is only once the surface has become contaminated by the presence of adsorbed P that the decomposition mechanism and kinetics change to allow the formation and desorption of H_2CO. The fact that the decomposition products and temperatures observed in our experiments are similar to those observed on Fe(110) suggests that the $(CH_3O)_3P$ decomposes via a mechanism similar to that on the contaminated Fe(110) surface.

The decomposition of the $(CH_3O)_3P$ is clearly activated by the presence of Fe on the SiC surface. In addition to generating decomposition products very much like those observed on Fe(110) the $(CH_3O)_3P$ deposits P onto the Fe/SiC surface. The Auger spectrum of the surface following decomposition is shown in figure 2(C) and clearly reveals the presence of a peak due to P at 119 eV.

The activity of the Fe-modified SiC surface towards $(CH_3O)_3P$ decomposition is certainly influenced by the amount of Fe on the surface. Figure 4 shows the H_2 TPD spectra from surfaces with varying amounts of Fe. The $(CH_3O)_3P$ was adsorbed using a saturation exposure and then heated at 2 K/s. The inset in figure 4 plots the peak area versus Fe : Si Auger intensity and reveals that the amount of hydrogen desorbing from the surface is increasing with the amount of Fe initially present on the surface. As mentioned earlier, it is not easy to establish an absolute Fe coverage from the Auger spectra. Nonetheless the data in figure 4 give some insight into the Fe coverage on the surface. It is only at Fe : Si Auger signal ratios in excess of 4 : 1 that the intensity of the hydrogen desorption feature begins to reach a plateau. This suggests that it is only at these Fe coverages that the film approaches complete coverage of the SiC surface. Figures 3 and 4 clearly show that $(CH_3O)_3P$ decomposition is due to the activation of the SiC surface by Fe. It seems reasonable that this should be a necessary condition for the activation of SiC surfaces for VPL, however, we have not yet made measurements of the frictional properties of these surfaces to demonstrate that the exposure of SiC surfaces to both $Fe(CO)_5$ and an organophosphate leads to reduced friction and wear. A VPL technique combining Fe deposition using $Fe(CO)_5$ with lubrication by an organophosphorus compound such as TCP could have widespread application in ceramic VPL and has distinct potential advantages over static activation methods [2,4,5].

3.4. The $(CH_3O)_3P$ decomposition mechanism on the Fe-modified SiC surface

The decomposition of $(CH_3O)_3P$ on the Fe-modified SiC surfaces appears to occur via a $CH_3O_{(ad)}$ intermediate. Such a mechanism is consistent with previous studies of $(CH_3O)_3P$ on the Fe(110) surface and is not surprising since on the Fe-modified SiC surfaces $(CH_3O)_3P$ is essentially reacting on the Fe overcoat [25]. The primary differences between the study on Fe(110) and the observations made in this work are that on the Fe-modified SiC surface we observe the desorption of H_2CO and CH_3OH in addition to the CO and H_2 observed on the clean Fe(110) surface.

The decomposition of $(CH_3O)_3P$ on the clean Fe(110) surface is deemed to proceed via a $CH_3O_{(ad)}$ intermediate which decomposes by β-hydride elimination to produce CO and H_2 desorption at 430 K [25]. The basis for this is that methanol (CH_3OH) is known to adsorb on the Fe(110) surface by deprotonation to form the $CH_3O_{(ad)}$ which then decomposes during heating to produce CO and H_2 with kinetics identical to those observed during $(CH_3O)_3P$ decomposition [38]. Although we do not yet have spectroscopic evidence for the formation of a $CH_3O_{(ad)}$ intermediate the fact that the decomposition products and kinetics for $(CH_3O)_3P$ on the Fe-modified SiC surface are so similar to those observed for CH_3OH and $(CH_3O)_3P$ on the Fe(110) surface makes a compelling case for the formation on $CH_3O_{(ad)}$ as a decomposition intermediate. The obvious difference between the Fe(110) surface and ours is that our Fe-modified SiC is not single crystalline and probably exposes adsorption sites that would be similar to those on a polycrystalline surface. Furthermore, our Fe surface is not completely clean and is probably modified by the presence of some oxygen and some carbon. It is known that on the Fe(100) surface the presence of oxygen can modify the $CH_3O_{(ad)}$ decomposition pathway such that in addition to producing CO and H_2 it generates H_2CO [39,40]. The fact that we observe the desorption of both H_2CO and CH_3OH suggests that the reaction mechanism is one in which $(CH_3O)_3P$ generates $CH_3O_{(ad)}$ intermediates which then either dehydrogenate by β-hydride elimination to produce H_2CO, CO, and H_2 or are hydrogenated to produce CH_3OH.

4. Conclusions

SiC surfaces can be activated for VPL by deposition of a thin layer of Fe through $Fe(CO)_5$ CVD. Enhanced decomposition of $(CH_3O)_3P$ indicates that these modified surfaces can react with organophosphorus compounds where the unmodified SiC surfaces do not. The decomposition mechanism of $(CH_3O)_3P$ on the Fe-modified SiC surface resembles that on single crystal Fe surfaces that have been modified by the presence of adsorbed P or O. This study has demonstrated a new procedure for use of volatile transition metal compounds to activate SiC and other ceramic surfaces such that they may be used in tribological applications that require high temperature VPL. This technique has the advantage that metal compounds can be delivered through the vapor phase in real time to maintain adequate surface reactivity for the growth of low friction polymers. Combined with real-time control of vapor phase lubricant delivery, the technique demonstrated in this work can help to achieve optimal lubrication of ceramic materials. This technique may be particularly important for the development of high-speed turbine engines and low heat rejection engines, where high temperature alloys and ceramic materials are primary components. However, $Fe(CO)_5$ itself is far from ideal for practical application due to its high toxicity and instability in air and under light. Future developments should explore more stable and less toxic transition metal compounds in order to provide safe and environment friendly activation of ceramic surfaces for vapor phase lubrication.

Acknowledgement

This work has been supported by the Air Force Office of Scientific Research under grant No. AF49620-98-100218.

References

[1] W. Liu, E.E. Klaus and J.L. Duda, Wear 214 (1998) 207.
[2] B. Hanyaloglu and E.E. Graham, Lubr. Eng. 50 (1994) 814.
[3] E.E Graham, A. Nesarikar, N. Forster and G. Givan, Lubr. Eng. 49 (1993) 713.
[4] B. Hanyaloglu and E.E. Graham, Tribol. Trans. 35 (1992) 77.
[5] J.F. Makki and E.E. Graham, Lubr. Eng. 47 (1991) 199.
[6] J.L. Lauer and S.R. Dwyer, Tribol. Trans. 33 (1990) 529.
[7] J.L. Lauer and S.R. Dwyer, in: *Proc. Jpn. Int. Tribol. Conf.*, Nagoya, Vol. II (Japanese Society of Tribologists, 1990) p. 989.
[8] J.F. Makki and E.E. Graham, Tribol. Trans. 33 (1990) 595.
[9] E.E. Klaus, G.S. Jeng and J.L. Duda, Lubr. Eng. 45 (1989) 717.

[10] J.C. Smith, M.J. Furey and C. Kajdas, Wear 181–183 (1995) 581.

[11] M. Groeneweg, N. Hakim, G.C. Barber and E. Klaus, Lubr. Eng. 47 (1991) 1035.

[12] B. Hanyaloglu, D. Fedor and E.E. Graham, Lubr. Eng. 51 (1995) 252.

[13] N.H. Forster, Tribol. Trans. 42 (1999) 1.

[14] N.H. Forster and H.K. Trivedi, Tribol. Trans. 40 (1997) 493.

[15] N.H. Forster and H.K. Trivedi, Tribol. Trans. 40 (1997) 421.

[16] W.G. Sawyer and T.A. Blanchet, Wear 225–229 (1999) 581.

[17] W. Morales, E.E. Graham and T. Galvin, Lubr. Eng. 53 (1977) 27.

[18] W.G. Sawyer and T.A. Blanchet, Wear 211 (1997) 247.

[19] H. Heshmat, Tribol. Trans. 34 (1991) 433.

[20] K.W. Van Treuren, D.N. Barlow, W.H. Heiser, M.J. Wagner and N.H. Forster, J. Eng. Gas Turbines Power 120 (1998) 257.

[21] D.P. Adams, T.M. Mayer, E. Chason, B.K. Kellerman and B.S. Swartzentruber, Surf. Sci. 371 (1997) 445.

[22] R.B. Jackman and J.S. Foord, Surf. Sci. 209 (1989) 151.

[23] J.S. Foord and R.B. Jackman, Chem. Phys. Lett. 112 (1984) 190.

[24] L. Sun and E.M. McCash, Surf. Sci. 422 (1999) 77.

[25] A.W. Holbert, J.D. Batteas, A. Wong-Foy, T.S. Rufael and C.M. Friend, Surf. Sci. 401 (1998) L437.

[26] Z.Y. Xie, S.F. Chen, J.H. Edgar, K. Barghout and J. Chaudhuri, Electrochem. Solid State Lett. 3 (2000) 381.

[27] X. Qizhen, Q.K. Xue, Y. Hasegawa, I.S.T. Tsong and T. Sakurai, Appl. Phys. Lett. 74 (1999) 2468.

[28] V. Ramachandran, M.F. Brandy, A.R. Smith, R.M. Feenstra and D.W. Greve, J. Electron. Mater. 27 (1998) 308.

[29] T. Tsukamoto, M. Hitai, M. Kusaka, M. Iwami, T. Ozawa and T. Nagamura, Surf. Sci. 371 (1997) 316.

[30] V. Van Elsbergen, T.U. Kampen and W. Mönch, Surf. Sci. 365 (1996) 443.

[31] L. Li and I.S.T. Tsong, Surf. Sci. 364 (1996) 54.

[32] L. Li and I.S.T. Tsong, Surf. Sci. 351 (1996) 141.

[33] D. Ren and A.J. Gellman, Tribol. Lett. 3–4 (1999) 191.

[34] D. Ren and A.J. Gellman, Surf. Sci., submitted.

[35] D. Ren and A.J. Gellman, Tribol. Int., submitted.

[36] L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach and R.E. Weber, *Handbook of Auger Electron Spectroscopy*, 2nd Ed. (Physical Electronics Industries Inc., MN, 1976).

[37] M.P. Seah and W.A. Dench, Surf. Interface Anal. 1 (1979) 2.

[38] T.S. Rufael, J.D. Batteas and C.M. Friend, Surf. Sci. 384 (1997) 156.

[39] J.P. Lu, M.R. Albert and S.L. Bernasek, Surf. Sci. 258 (1991) 269.

[40] J.P. Lu, M.R. Albert and S.L. Bernasek, Surf. Sci. 218 (1989) 218.