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ACTIVATION OF SiC SURFACES FOR VAPOR PHASE LUBRICATION BY CHEMICAL VAPOR DEPOSITION OF FE

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ABSTRACT

Vapor phase lubrication (VPL) has been proposed as a method for lubricating high temperature engines. During VPL, lubricants are delivered through the vapor phase to high temperature engine parts and react on their surfaces to deposit a thin, solid, lubricating film. Although ceramics such as SiC are desirable materials for high temperature applications, their surfaces are unreactive for the decomposition of TCP and thus not amenable to vapor phase lubrication. As a means of activating the SiC surface for TCP decomposition we have used chemical vapor deposition of Fe from $\text{Fe}(\text{CO})_5$. Modification of the SiC surface with adsorbed Fe accelerates subsequent decomposition of TCP and deposition of P and C onto the surface. In the temperature range 500 - 800 K, *m*-TCP decomposes more readily on Fe-coated SiC surfaces than on SiC surfaces. The C and P deposition rates depend on the thickness of the Fe film and are further enhanced by oxidation of the Fe. This work provides a proof-of-concept demonstration of the feasibility of using vapor phase lubrication for ceramics.

INTRODUCTION

The development of high efficiency engines operating at extremely high temperatures requires the use of lubricants that can endure temperatures over 800 K. Traditional liquid lubricants have a temperature limit of 650 K. Solid lubricants can be used, but are limited by the lack of a mechanism for replenishment following sliding wear. In order to overcome these difficulties, vapor phase lubrication (VPL) has been proposed as a method for the lubrication of high temperature engine components [1, 2]. In this method, a vapor lubricant is continuously delivered by a carrier gas to hot engine components and reacts on their surfaces to deposit a thin, solid, lubricating film which protects the engine surfaces from sliding wear. The most widely studied vapor phase lubricants are phosphorous containing organics, including *aryl*phosphates such as tricresylphosphate (TCP), $(\text{CH}_3\text{-C}_6\text{H}_4\text{O})_3\text{P=O}$. These phosphates are thought to function by decomposing on reactive metal surfaces, such as Fe and Cu, to form polyphosphate films

which contain small graphitic particles. The resulting carbon/phosphorus film provides effective lubrication. Ceramic materials should be ideal materials for high temperature engine applications because they have many desirable high temperature properties. Lubrication of ceramics through the vapor phase or otherwise is, however, a difficult problem. Ceramics are chemically inert and as a consequence lubricants do not react readily on their surfaces. One solution to this problem might be to activate ceramic surfaces with Fe or other metals which are known to react with vapor lubricants such as TCP [3]. The work presented in this paper demonstrates the feasibility of activating SiC surfaces for *m*-TCP decomposition by using $\text{Fe}(\text{CO})_5$ for chemical vapor deposition of Fe. During steady state exposure to the surface at high temperature *m*-TCP is shown to decompose more readily on Fe/SiC surfaces than on clean SiC surfaces. The C and P deposition rates depend on the thickness of the Fe film and are accelerated by oxidation of the Fe. This work provides a proof-of-concept demonstration of the feasibility of using Fe CVD in conjunction with TCP for vapor phase lubrication of ceramics.

EXPERIMENTAL

All experiments were conducted in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure of 10^{-10} Torr. The chamber was equipped with an ion sputter gun, a quadrupole mass spectrometer (QMS), and a cylindrical mirror analyzer (CMA).

RESULTS AND DISCUSSION

Temperature programmed reaction spectroscopy has been used to probe the mechanism of *m*-TCP decomposition on the clean SiC surface and the Fe/SiC surface. Figure 1 illustrates the TPR spectra of one monolayer of *m*-TCP on the clean SiC surface. *m*-TCP itself has ionization fragments at $m/q = 91$ ($\text{CH}_3\text{C}_6\text{H}_4^+$), 92 ($\text{CH}_3\text{C}_6\text{H}_5^+$) and 107 ($\text{CH}_3\text{C}_6\text{H}_4\text{O}^+$). The desorption features at 260 K indicate molecular desorption of *m*-TCP. The broad desorption peaks at 645 K for fragments with $m/q = 91$ and 92 reveal toluene desorption. This result

suggests that on the SiC surface, some *m*-TCP desorbs molecularly while the remainder decomposes through C-O bond scission to form tolyl groups which can be hydrogenated to toluene at $T = 645$ K.

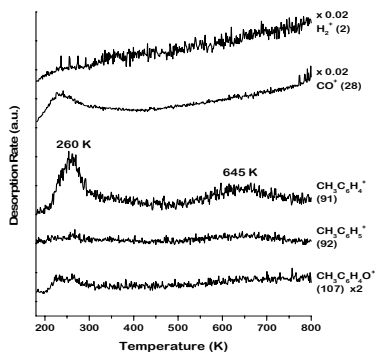


Figure 1. TPR spectra of *m*-TCP on the SiC surface for ionization fragments with $m/q = 2$ (H_2^+), 28 (CO^+), 91 ($CH_3C_6H_4^+$), 92 ($CH_3C_6H_5^+$) and 107 ($CH_3C_6H_4O^+$). The *m*-TCP coverage was ~ 1 ML. The sample heating rate was 2 K/s. On the SiC surface, some *m*-TCP desorbs molecularly at 260 K, while the remainder decomposes through C-O bond cleavage to produce tolyl intermediates, $CH_3C_6H_4^+$, which are hydrogenated to desorb as toluene at $T = 645$ K.

The TPR spectra of *m*-TCP on the Fe/SiC surface shown in Figure 2 are clearly different from the TPR spectra of *m*-TCP on the clean SiC surface. Toluene evolves into the gas phase over a temperature range of 300 – 500 K, while CO desorbs over the temperature range 300 – 450 K. There is a small H_2 desorption peak observed at 560 K. On the Fe/SiC surface the majority of the *m*-TCP decomposes through C-O bond cleavage to form tolyl intermediates which can be hydrogenated to toluene at $T = 300 - 500$ K. Subsequently, tolyl groups decompose further to C_xH_y fragments, which desorb as H_2 and CO at 600 – 800 K.

In order to demonstrate the potential for use of Fe modification as a means of activating the SiC surface for vapor phase lubrication, we have studied the uptake of C and P onto the surface during exposure to *m*-TCP. The experiments were performed using two different Fe film thicknesses on the SiC surfaces and exposing these to *m*-TCP at three different temperatures (500 K, 650 K, and 800 K). Figure 3 shows the thickness of C/P film during exposure of clean SiC, Fe/SiC, and O/Fe/SiC surfaces to *m*-TCP at 500 K.

The C/P film thickness curves clearly reveal two trends in the deposition rates. The rate of film thickness onto the Fe/SiC surfaces is significantly greater than on the clean SiC surface and increases with Fe coverage indicating that the activity of the surfaces for decomposition of *m*-TCP follows the order:

$$\text{clean SiC} < \text{Fe}_{1.0 \text{ \AA}}/\text{SiC} < \text{Fe}_{1.8 \text{ \AA}}/\text{SiC}.$$

What is more interesting is the fact that the rates of deposition onto the oxidized Fe/SiC surfaces are greater than onto the clean SiC and the Fe/SiC surfaces indicating that the activity for decomposition of *m*-TCP follows the order:

$$\text{clean SiC} < \text{Fe/SiC} < \text{O/Fe/SiC}$$

The *m*-TCP decomposition experiments illustrated in Figure 3 have also been performed at surfaces temperatures of 650 K and 800 K. The uptake curves obtained at those temperatures reveal the same relative reactivities of the different surfaces.

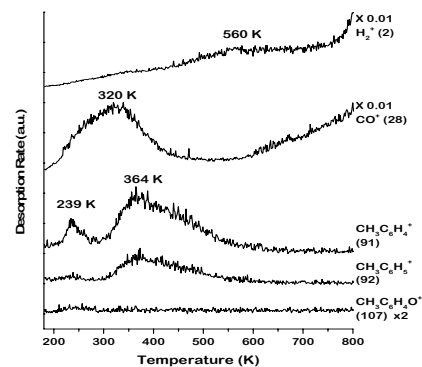


Figure 2. TPR spectra of *m*-TCP on the Fe/SiC surface for ionization fragments with $m/q = 2$ (H_2^+), 28 (CO^+), 91 ($CH_3C_6H_4^+$), 92 ($CH_3C_6H_5^+$) and 107 ($CH_3C_6H_4O^+$). The sample heating rate was 2 K/s. On the Fe/SiC surface, a little *m*-TCP undergoes molecular desorption, while the majority decomposes through C-O bond scission to form tolyl intermediates, $CH_3C_6H_4^+$, which are hydrogenated to desorb as toluene at $T = 300 - 500$ K.

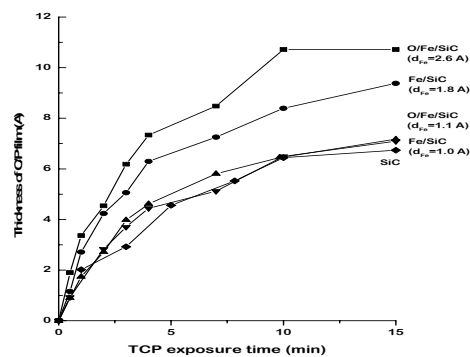


Figure 3. The increase in the C/P film thickness on the O/Fe/SiC ($d_{Fe}=2.6$ Å), Fe/SiC ($d_{Fe}=1.8$ Å), O/Fe/SiC ($d_{Fe}=1.1$ Å), Fe/SiC ($d_{Fe}=1.0$ Å) and clean SiC surfaces as a function of *m*-TCP exposure while heating the surfaces at 500 K. The growth rate of the C/P film thickness is indicative of the *m*-TCP decomposition rates on the different surfaces. The film thickness is estimated from the attenuation of the Si Auger signals before and after TCP reactions.

CONCLUSIONS

Thin Fe films can be deposited on the surface of SiC by exposure to $Fe(CO)_5$ with the surface at a temperature of ~ 600 K. Once activated by the deposition of Fe, the SiC surfaces will decompose vapor phase lubricants such as *m*-TCP. The Fe/SiC surface is further activated by oxidation of the Fe film. These results suggest that surface activation by Fe CVD might be a viable approach to the vapor phase lubrication of ceramics.

ACKNOWLEDGMENTS

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