CHEMICAL VAPOR DEPOSITION APPLICATIONS IN THIN-FILM COATINGS FOR HIGH TEMPERATURE LUBRICATION

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ABSTRACT:

In the design of high-speed engines whose operating temperatures often exceed 400°C, the choice of a lubricant and lubrication technique is of considerable concern. The method chosen to lubricate the contact surfaces must be effective in reducing friction and increasing the usable life of these components. Liquid lubricants provide excellent protection at low temperatures, but at temperatures above 250 °C traditional liquid lubricants break down and cannot be used. A number of mechanisms of lubrication at high temperatures exist, including solid, powder, catalytic lubrication and tribo-polymerization. Work at the Advanced Manufacturing Center at Cleveland State University and research performed at Wright-Patterson Air Force Base has produced novel techniques for forming lubricating films on ceramics using a vapor-delivered lubricant. This paper focuses on the formulation of a deposition model to study a chemical vapor deposition (CVD) mechanism to produce lubricating films on cast-iron as the most promising new technology for high temperature applications. Vapor phase deposition produces a protective film that is stable at high temperatures above 300 °C. This film provides a lubricating environment that has the ability to significantly reduce the coefficient of friction. At these high temperatures, no other method of lubrication is capable of providing such low values of coefficient of friction and/or enabling wear control. Wear and friction studies have indicated the formation of an iron phosphate film that catalyzes the formation of a protective lubricating film. Protective films were grown by CVD in a Thermal Gravimetric Analyzer (TGA) setting. Kinetic analysis of these data was used to formulate a film deposition model that can be used for the estimation of both kinetic and transport parameters. Statistical analysis of the experimental data yields transport and kinetic parameters that complement the proposed model. The model can be reliably used as a predictive and scale-up tool.

INTRODUCTION

Lubrication is the introduction of a substance between the contact surfaces of moving parts to reduce friction and wear. The lubricant used may be gaseous, liquid or solid. Liquid lubricants provide excellent effects at low temperatures. When engines and aircrafts are operated at high speeds to obtain greater efficiency, the engine lubrication system must be made operable at high temperature levels say above 250° C. Difficulties that can be expected at these temperatures are lubricant oxidation, thermal instability and high volatility. Due to the thermal limits of conventional liquid lubricants, there is a demand for high temperature lubrication alternatives. The relative ease of vapor delivery systems has made the vapor phase lubrication (VPL) an extremely attractive technique over the past decade. In vapor phase lubrication, an organic liquid is vaporized and covered by a gaseous stream that impinges on the surface that is to be lubricated. This organic vapor then reacts with the surface to form a lubricious deposit. Klaus and co-workers[1] studied the structure of films formed on iron foil and silicon carbide wafers using tricresyl phosphate(TCP) and poly phenyl ether(PPE) at 700°C. Vapor phase lubrication studies on a variety of metallic substrates have indicated the need for a transition metal to be present in order for a film to be deposited successfully[2, 3, 4]. The chemical reaction between the lubricant and iron surface is said to be catalyzed by the presence of the transition metal to generate an iron phosphate film[1]. This lubrication method has been successfully applied to metals at high temperatures[5, 6]. Makki and Graham[6] studied TCP and postulated a mechanism for the deposition of TCP from vapor phase on different surfaces including metals, quartz and ceramics to produce tenacious polymeric films with a nodular structure. While their studies and results were exciting, the ortho-isomer of TCP is a known neurotoxin. Aiming to overcome the potential dangers associated with TCP, Rao[7] investigated an alternative vapor phase lubricant called Bis-(4-flurophenoxy)-tetrakis-(3-trifluromethylphenoxy) clyclotriphosphazene(X-1P)**.** X-1P provided adequate lubrication and was shown to work at temperatures higher than those used for TCP. However, at high temperatures X-1P forms hydrogen fluoride and corrodes metallic parts over extended operation.

In response to health and environmental concerns, "synthetic" analogues to the natural esters were developed to reduce both toxicological concerns and production costs. Due to its chemical similarity with TCP (cf. fig1 and 2), the alternative lubricant used for this research was tert-butylphenyl phosphate (TBPP). Phosphate esters in the vapor phase have shown that, under the right conditions, it can produce a lubricating film that is stable at very high temperatures[3, 4, 8]. This film provides lubrication and has the ability to significantly reduce the coefficient of friction for operating temperatures above 300°C. This particular feature of TBPP was recently demonstrated by Desai[8], by using a universal wear tester machine (UWTM) to evaluate the performance of the lubricant under actual dynamic conditions.

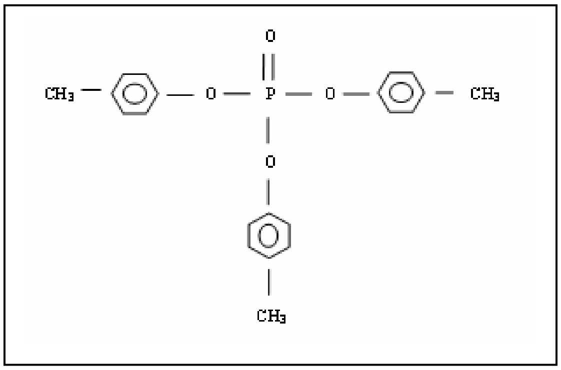

Figure1: Chemical structure of TCP

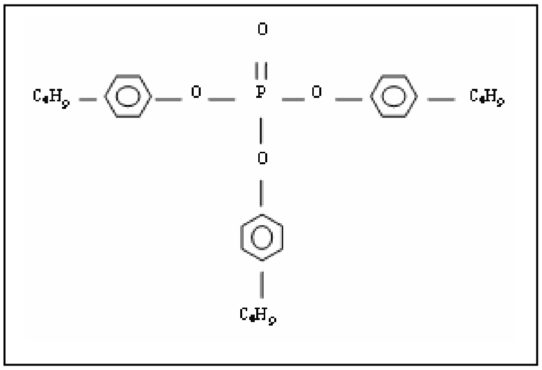

Figure 2: Chemical structure of TBPP

This paper focuses on the formulation and validation of a model to describe the chemical vapor deposition (CVD) experiments in a modified TGA environment. Protective films were grown by CVD in the TGA setting for temperatures ranging between 270-330°C. Kinetic analysis of the TGA data indicates that a film deposition model can be used for the estimation of both kinetic and transport parameters. The characterization of the deposited film was carried out by elemental surface analysis through energy dispersive x-ray analyzer (EDXA), Auger electron spectroscopy (AES), and Fourier Transform Infrared Spectroscopy (FTIR, film elemental composition).

EXPERIMENTAL

Materials

The lubricant used for this research was a tert-butylphenyl phosphate (TBPP) manufactured by GLCC Corporation. TBPP possesses superior oxidative, thermal and hydrolytic stability compared to all other commercial phosphate ester products. Its extremely low volatility and exceptional stability makes TBPP an excellent choice for high temperature applications where an ashless additive is desired. It can be effective and highly stable anti-wear additive in both petroleum and synthetic base stocks including polyesters, diesters and polyalphaolefins. It is known to be nontoxic and it has no halogen in its structure, which might lead to corrosion.

Equipment

The formulation of a deposition environment to study the chemical vapor deposition (CVD) mechanism was achieved by modifying a thermal gravimetric analyzer (TGA), which acts as a hot wall closed reactor. The cast iron was shaped into a cylindrical structure, which was then suspended from the quartz rod within the hot wall reactor. The lubricant was placed in a sample pan positioned on the inside bottom of the furnace. During this research the amount of lubricant used was varied by using one to three sample pans. The locations of the pans were also varied to examine the effects of location in producing thicker films. The sections of the quartz furnace tube that were not in contact with the furnace were shielded with aluminum foil to avoid or minimize solution condensation. No purge gas was used during the experiments to maximize the time of the reactants remained inside the chamber.

MODEL FORMULATION

A schematic of the film deposition process model is shown in Figure 3. The precursor is vaporized and these vapors react with the cast-iron sample leading to the formation of a thin deposit. Subsequent reaction requires that the reactants diffuse through the film to reach the reaction surface. Thus the process involves three steps: transportation of the aryl phosphate species from the bulk gas to gas/film interface, diffusion through the growing film towards the substrate surface and a heterogeneous reaction between the substrate and the diffusing species.

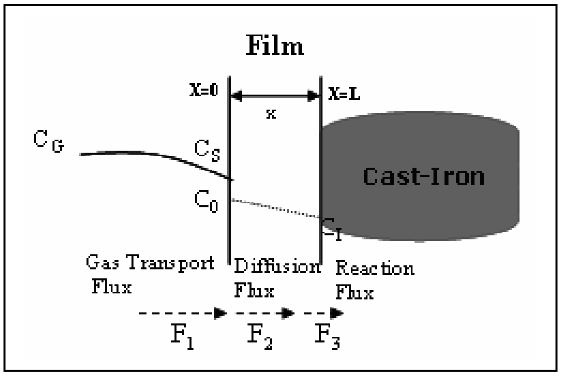

Figure 3: Model of film deposition process

Where mathematical formulation would be:

$$F_1 = k_m\left(C_G - C_S\right) \qquad F_2 = -D\frac{dC}{dx} \qquad F_3 = \frac{K_r C_I^n}{S_a}$$

Here C_G is the concentration of the aryl ester phosphate in the bulk gas, C_o is the concentration of the aryl ester phosphate just inside the film surface, C_I is the concentration of the aryl ester phosphate at the iron/film interface, C_S is the concentration of the aryl ester phosphate at the outermost layer of film, D is the diffusivity of the aryl ester phosphate in the film , k_m is the gas phase mass transfer coefficient , k_r is the rate constant for the surface chemical reaction, S_a is the specific surface length (Area of the iron rod/Volume of the TGA), L is the film thickness, and *n* is the overall reaction order.

If the diffusion characteristic time is comparatively smaller than that of the reaction, the boundaries will behave as if they were stationary on the diffusion time scale. This permits us to make a quasi-steady state approximation to simplify the governing equations; i.e. diffusion and reaction are occurring in a film of constant thickness.

Under quasi-steady state conditions, the mathematical model reduces to the simple diffusion model

$$\frac{d}{dx}\left[D\frac{dC}{dx}\right] = 0 \qquad [1]$$

Subject to the following boundary conditions:

$$k_m\left(C_G - C_S\right) = -D\frac{dC}{dx} \qquad at\ x = 0 \qquad [2]$$

$$-D\frac{dC}{dx} = \frac{k_r C_I^n}{S_a} \qquad at\ x = L \qquad [3]$$

where $\frac{(C_o - C_I)}{L}$ was substituted for $\frac{dC}{dx}$

Integrating Eq [1] using boundary conditions yields,

$$C(x) = C_o - \left[\frac{K_r}{DS_a} C_I^n \right] x \qquad [4]$$

The quasi-steady state condition, $F_1 = F_2 = F_3$ leads to,

$$\left[1 + \frac{k_r}{h_G S_a} C_I^{n-1} + \frac{k_r L}{DS_a} C_I^{n-1} \right] C_I = C^* \qquad [5]$$

$$\left[1 + \frac{k_r}{h_G S_a} C_I^{n-1} + \frac{k_r L}{DS_a} C_I^{n-1} \right] C_o = \left[1 + \frac{k_r L}{DS_a} C_I^{n-1} \right] C^* \qquad [6]$$

where C^* is the concentration of the aryl ester phosphate in the film in thermodynamic equilibrium with the gas phase and h_G is the gas phase mass transfer coefficient.

The rate of deposition can now be related to the growth rate of the solid film by a simple mass balance, i.e.,

$$RM_w = \rho \frac{dL}{dt} \approx \frac{dL}{dt} = \frac{M_w}{\ell S_a} \left(\frac{k_r C^*}{\dfrac{1}{C_I^{n-1}} + \dfrac{k_r L}{DS_a}} \right) \qquad [7]$$

subject to the boundary condition L=0 at t=0

where $R = \frac{k_r C_I^n}{S_a}$, M_w and ℓ are the Molecular weight and density of the film, respectively. For the typical deposition conditions, one can safely assume that the mass transfer from the gas phase to the film /substrate interface is fast as compared to reaction, and then k_m is sufficiently large $\left(i.e \frac{k_r}{(k_m / HRT)} = \frac{k_r}{h_G} << 1 \right)$.

Eq [7] can be integrated to yields,

$$t - t_0 = \frac{\ell S_a}{M_w k_r C^* D} \left[\frac{D}{C_I^{n-1}} (L - L_0) + \frac{k_r}{2S_a} (L^2 - {L_0}^2) \right] \qquad [8]$$

Where Eq. [8] is rewritten in terms of weights to better correlate with the TGA experimental data. i.e., by substituting $W = \ell * A * L$ (where A is the area of the film), we obtain

$$t - t_o = \frac{S_a}{M_w k_r C_I^{n-1} C^* A} (W - W_o) + \frac{1}{2DM_w C^* \ell A^2} (W^2 - W_o^2) \qquad [9]$$

or

$$\frac{t - t_O}{W - W_O} = \frac{\tau_R}{W^*} + \frac{\tau_D}{(W^*)^2} (W + W_O) \qquad [10]$$

where, $\frac{1}{2M_w C^* D\ell A^2} = \frac{\tau_D}{(W^*)^2}$, $\frac{S_a}{M_w k_r C_I^{n-1} C^* A} = \frac{\tau_R}{W^*}$, W_o is the initial weight of the coupon and W^* is a reference weight.

RESULTS AND DISCUSSION

The formulation of a deposition environment to study the chemical vapor deposition mechanism was achieved through a TGA. Each experiment was carried out by using a cast-iron substrate with a 50-minute isothermal region. The 50-minute isothermal region was chosen from experience as it proved to be long enough to result in films of appreciable weight at lower temperatures.

Data pre-conditioning

The isothermal data must be analyzed statistically after the completion of each thermo-gravimetric (TGA) experiment before proceeding with the kinetic analysis. The experimental points that correspond to the isothermal region can be easily identified from the experimental data, cf. fig.4

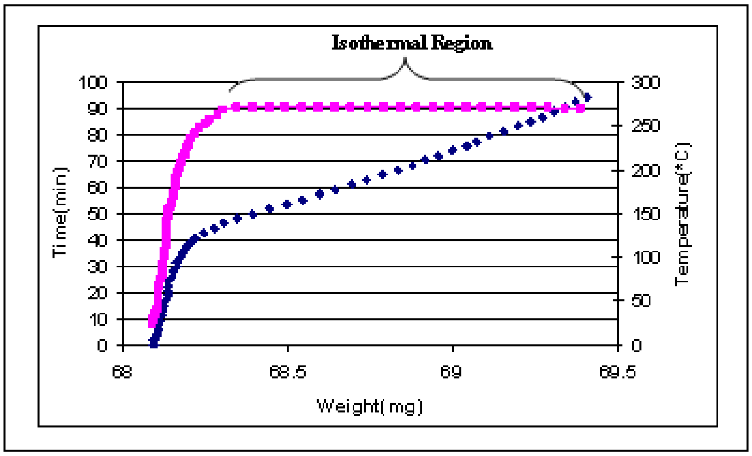

Figure 4: Isothermal region data

The kinetic and transport parameters can now be easily obtained by Least-Squares method. The transition from the reaction control regime (constant ordinate) to the diffusion control regime (linear correlation) can be determined via one-sided sensitivity analysis. This analysis is illustrated in fig. 5.

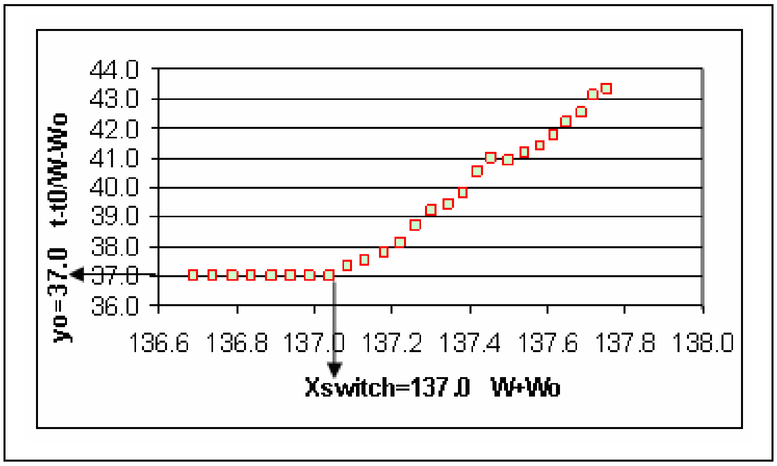

Figure 5: Identifying the “switch” point through one-sided sensitivity analysis.

Kinetic Analysis

Using the data obtained at various temperatures, the activation energy and frequency factor can be obtained by Least-Squares method applied to an Arrhenius plot (cf. fig 6).

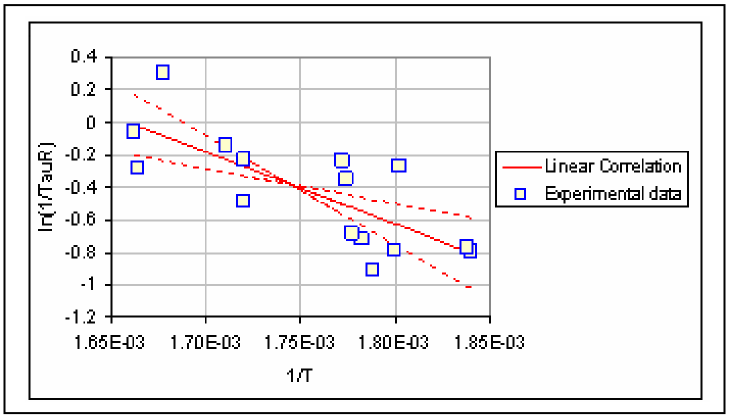

Figure 6: Arrhenius plot to calculate Activation Energy for reaction

The activation energy (slope) was determined to be 8.8 kcal/mol ± 4.5 kcal/mol. This apparent activation energy is in very close agreement with data reported in the literature by Makki and Graham[6].

Energy Dispersive X-ray Analyses (EDXA)

The films deposited on cast-iron were characterized by Energy Dispersive X-ray Analysis (EDXA). Table 1 shows the EDXA results for films obtained at different temperatures.

Table 1: EDXA results for films deposited on cast-iron foils

Element	Before deposition	275 °C	280 °C	290 °C	330 °C
C	0	9.44	10.32	12.06	14.07
O	0.94	10.36	11.97	14.52	23.9
P	0	0.43	0.83	1.10	3.81
Fe	99.06	79.76	76.89	72.32	58.22

The results suggest that as temperature increases a thicker film is created. For example, for the same amount of lubricant used at 275 °C and 280 °C, the phosphorus approximately doubled. Also, for experiments from 290 °C to 330 °C the phosphorus increased three and a half times while the lubricant mass was only 25% larger at these temperatures.

Auger Electron Spectroscopy (AES)

Auger electron spectroscopy was utilized to investigate the film chemistry. Figures 7 and 8 show the atomic percentage of carbon, oxygen, iron, and phosphorus as a function of depth of the film for low and high temperature deposition. For a 16 mg sample used for deposition experiments at 270 °C, the phosphorous atomic percentage becomes negligible after 135 nm.

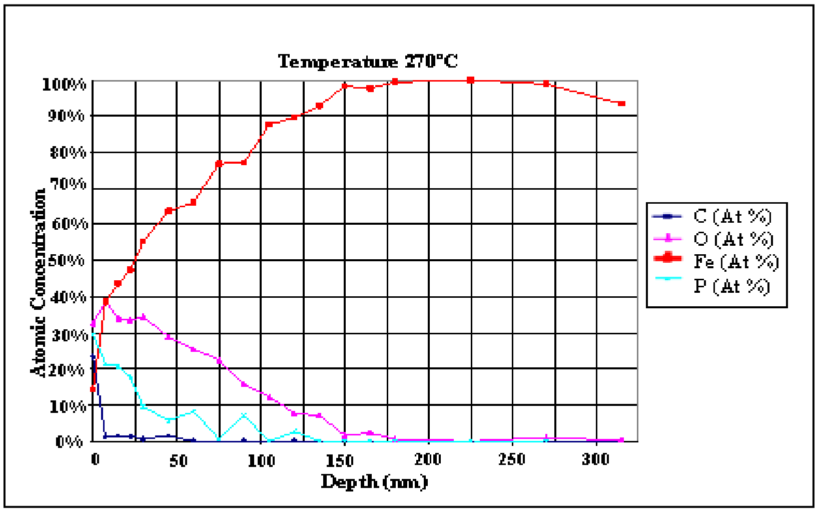

Figure 7: AES depth profiling for a film deposited at 270 °C

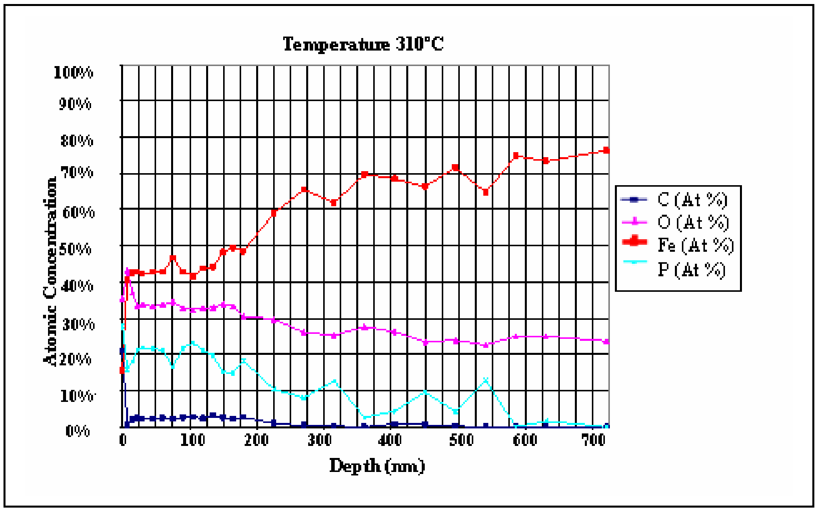

Figure 8: AES depth profiling for a film deposited at 310 °C

However, for films deposited at 290 °C and 310 °C from 26 mg of lubricant, the phosphorous becomes noticeable up to a depth of 225 nm and 720 nm, respectively. There is a small amount of carbon in the outer layer of each of these samples. Artifacts resulting from the low sensitivity of the AES to the phosphorous and the noise in the spectrum are more noticeable, as the atomic percentage of P becomes smaller.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was utilized to identify the main functional groups in the film deposition process. Figure 9 shows the spectrum for a film deposited at 275 °C. The sloping baseline observed in the spectra is a result of surface roughness and reflectivity difference between the gold slide used as a background and the cast-iron substrate. Spectra for foils treated below 275 °C appear similar to that of bare cast-iron, which would signal these experiments as corresponding to the thinnest films generated.

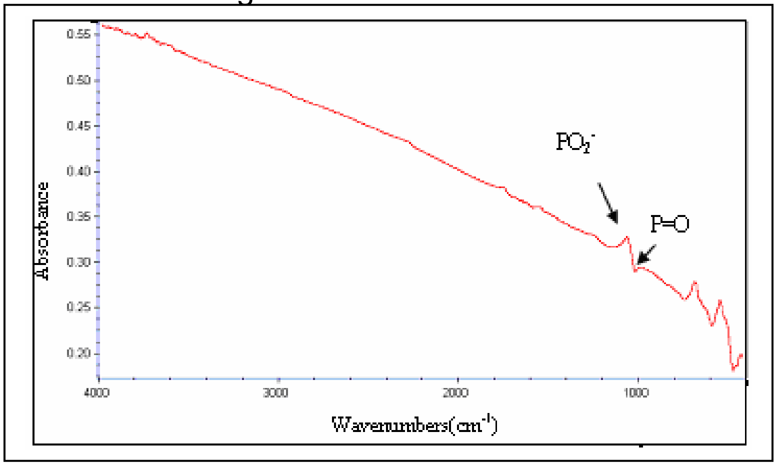

Figure 9: Infrared spectrum of a film deposited on cast-iron at 275 °C

The spectra for experiments where successful deposition occurred did not show any aromatic C-H stretches, which suggests that the outermost film layers do not have any aryl groups. This means that either the aryl phosphate ester decomposes when being heated and only the phosphate anion PO_4^{-3} reacts with the iron surface or that the aryl molecule reaches the iron surface and upon reaction the aryl group decomposes. As the deposition temperature increased, the P=O peak becomes more prominent. In addition an extra peak corresponding to P-O-C becomes visible as the temperature increases (cf. fig. 10). These observations corroborate the AES analysis that as the deposition temperature increases, thicker films are generated.

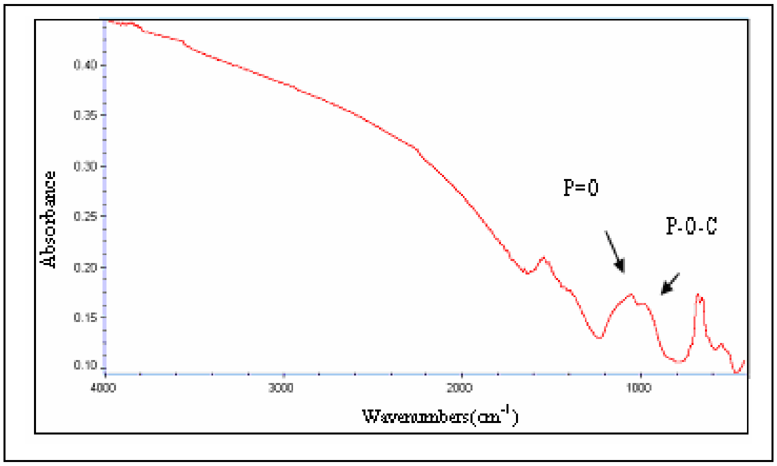

Figure 10: Infrared spectrum of a film deposited on cast-iron at 310 ^{o}C

CONCLUSIONS

A modified TGA Equipment was successfully used to grown lubricating films on cast iron foils by chemical vapor deposition. Deposition experiments produced films for temperatures ranging between 270-330^{0} C using a tert-butylphenyl phosphate as a precursor. The TGA arrangement enables monitoring deposition experiments under controlled conditions and at constant temperature. Studies were restricted to temperatures corresponding to conditions that have shown one order of magnitude reductions in the coefficient of friction. Experimental data collected in this experimental setting can be efficiently used to estimate kinetic and transport parameters that describe the deposition and possible vapor-phase lubrication mechanism. The ability to control the temperature during the deposition experiments, yields reliable estimations of the temperature dependence of transport and kinetic parameters assumed to follow an Arrhenius dependence on temperature. Since the ability to grow thicker films correlates directly with temperature, this model allows identifying critical parameters in scale-up studies of the process.

EDXA elemental analysis showed that as deposition temperature increases, the iron content of the substrate decreases while the phosphorus content increases. AES analysis indicates that as the deposition temperature increases so does the atomic percentage of phosphorous. FTIR analysis reveals that the outermost film layer does not have any aryl group suggesting that aryl phosphate ester decomposes when being heated.

ACKNOWLEDGMENTS

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