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RESEARCH ARTICLE

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ZTMD Flow Profiles in Sub-Monolayer Film Thickness Regime

Abstract:

Lubricant reflow for ZTMD is characterized in the sub-monolayer film thickness regime between 2 and 12 Å. The thickness-dependent diffusion constant, D(h), is quantified. Fickian diffusion using the experimental D(h) values are then used to numerically simulate lubricant flow. A surface viscosity of 300 Pa.s is estimated from the flow profiles.

Keywords: ZTMD; hard disk drives; lubricant flow; diffusion.

Introduction:

The reflow kinetics of the boundary perfluoropolyether (PFPE) lubricant Z-Tetraol in a trough as might be created under heat-assisted magnetic recording (HAMR) conditions were investigated recently [1, 2]. Fickian diffusion based upon an experimental thickness-dependent diffusion coefficient was used to numerically simulate lubricant reflow into laser-depleted troughs as a function of trough number and adjacent trough distances, trough depth, trough width, and duty cycle (reflow time between successive laser exposures). The results of the numerical simulations indicated that trough recovery by reflow increased with increasing duty cycle or decreasing number of adjacent troughs, trough separation distance and laser depletion rate. Reflow rates were computed to slow significantly when closely spaced multiple troughs coalesced to behave like a single, larger trough. These data indicated that conclusions based upon a single laser trough could be misleading when extrapolated to real HAMR conditions [1, 2].

The perfluoropolyether "ZTMD" continues to be widely studied because of its unique chemical structure and its resultant boundary film properties [3, 4]. By containing pendant polar functional groups in the middle of the main chain that are capable of interacting with the underlying substrate, a more solid-like 2-dimensional film characterized by low mobility and a larger Hamaker constant is realized [4]. These features produce a boundary lubricant film that is more resistant to the disturbing effects of a low-flying slider. However, in HAMR applications that could require reflow as a possible healing mechanism for laser-induced thickness depletion, low mobility lubricant films like ZTMD may be at a disadvantage.

In order to assess the effect of lubricant mobility on reflow in laser-induced lubricant troughs, we investigate herein the flow characteristics of sub-monolayer ZTMD films on carbon surfaces. The thickness-dependent diffusion coefficient D(h) is determined from ZTMD flow experiments as a function of film thickness in the sub-monolayer regime between 2 and 12 Å. Flow is then simulated using D(h) and compared to experiment.

MATERIALS AND METHODS

ZTMD, Fig. 1, was synthesized from Z-Tetraol (1200 daltons) as described previously [3]. Z-Tetraol was purchased from Solvay-Solexis (Italy) as the GT grade (narrowly distributed molecular weight) and used directly. NMR (BrukerAvance 500 MHz spectrometer) data indicates a number average molecular weight of 2950 daltons.

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Rigid magnetic media were used as the substrates to study the topically-applied PFPE thin films. First, a cobalt-based magnetic recording layer (CoPtCr) was sputter-deposited onto smooth glass substrates. Next, 30 Å of a CVD nitrogenated amorphous carbon film was deposited. The carbon film thickness was quantified by Auger (Perkin-Elmer PHI 660 Scanning Auger Microprobe). For simplicity, this carbon film is referred to as "CNx" throughout this work. The carbon surface had a RMS roughness R_q = 0.3 nm, as measured by AFM (Digital Instruments Dimension 5000). Finally, the ZTMD lubricant films were applied to the carbon surfaces from solvent using a standard dip-coating methodology, using a typical concentration of 0.01 g/liter and a typical disk withdrawal rate of several mm/sec.

The thicknesses of the topically applied ZTMD films were quantified by specular reflection FTIR (Nicolet Magna Model 560). The FTIR absorption band maximum was correlated to film thickness by XPS (Phi Quantum 2000 ESCA System) using a takeoff angle of 45° and an electron mean free path of 25 Å [5]. The FTIR-ESCA thickness correlation is shown in Fig. 2.

Lubricant flow as a function of time was investigated ellipsometrically using half-dipped ZTMD films as shown in Fig. 3. An optical surface analyzer (OSA) using both s- and p-polarized light was employed to directly image the disk surface for evidence of lubricant flow [6]. The Q polarized wave (phase contrast signal between the p- and s-polarized light) provided the highest sensitivity to changes in the lubricant film. The changes in the reflectivity were related to film thickness by calibrating the OSA to the FTIR film thicknesses, Fig. 2. The methodology used to extract flow distance versus time is shown in Fig. 3.

The ZTMD bonded fractions for the films used in the flow experiments were measured at the beginning and the end of the flow experiments. The initial bonded fractions were measured on sister disks while the final bonded fractions were measured on the experimental disks after completion of the flow experiments. During the course of the flow experiments, the bonded fraction increased from approximately 0.8 to 0.9. Because of the high initial bonded fraction, changes in the bonded fraction for ZTMD during the course of the flow experiments were not considered to be significant as the flow kinetics reasonably fit Eq. 3 below.

Lubricant flow was simulated by writing a Fortran computer code based on Fick's second law for diffusion in one dimension using a thickness-dependent diffusion coefficient.

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial h}{\partial x} \right) \qquad (1)$$

D is the diffusion coefficient, h is the lubricant film thickness, x is the distance, and t is time. The derivatives are approximated by finite differences using the *Forward Time, Centered Space* or FTCS approximation [7]. In the FTCS approximation, the time step is defined by the von Neumann stability condition, Eq. 2.

$$\Delta t \leq \frac{\Delta x^2}{2D} \qquad (2)$$

Results and Discussion:

Experimental flow profiles for sub-monolayer ZTMD films on CNx are shown in Figs. 4, 5. Figs. 4a, 4b, 4c, 5a, 5b and 5c correspond to 11.7, 10.9, 9.2, 6.5, 4.4 and 2.2 Å, respectively. The experimental data are discussed first. The diffusion process is characterized through the scaling of the mean square displacement with time using the completely general Eq. 3.

$$x^2 \propto t^{\gamma} \qquad (3)$$

x is the distance and t is the time. Plotting Eq. 3 as log $\langle x^2 \rangle$ versus log t provides the experimental way to determine the type of diffusion occurring in a given system. When $\gamma = 1$ normal diffusion is observed. Diffusion is anomalous for $\gamma \neq 1$. For $\gamma < 1$, trapping effects become dominant and sub-diffusion is observed [8]. For ZTMD films between 2 and 12 Å, Fig. 6a indicates an

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average value for γ = 1.11 ± 0.35 and thus lubricant flow will be treated as normal diffusion. The experimental diffusion coefficient as a function of film thickness, D(h), is summarized in Table 1 and plotted in Fig. 6b. The polynomial fit to the experimental data points, Eq. 4, is used in all of the simulations here.

$$\text{Log } D(h) = -15.99 + (0.25)(h) + (-0.0081)^2(h^2) \qquad (4)$$

h is the film thickness in Angstroms and D(h) is m^2/sec. Eq. 4 describes the isothermal flow of ZTMD at room temperature only.

The experimental D(h) represented by Eq. 4 may be compared to Eq. 5 and 6 below for the calculation of sub-monolayer D(h) based on the disjoining pressure gradient [9, 10]. Eq. 6 differs from Eq. 5 primarily by a correction for decreasing lubricant film density with decreasing film thickness.

$$D(h) = \frac{Ah^3}{6\pi\mu(h + d_o)} \qquad (5)$$

$$D(h) = \frac{A}{18\pi\mu_o h_m} \frac{\left(H - \frac{D_o}{2}\right)H^3}{(H + D_o)^4} \left(1 - \frac{\alpha_n H}{4} + \frac{\alpha_n{}^2 H^2}{10}\right) \qquad (6)$$

A is the Hamaker constant, and μ represents a surface viscosity. In Eq. 5, h and d_o are the film thickness and cut-off distance, respectively. In Eq. 6, $H = h/h_o$, where h_o is the initial film thickness; $D_o = d_o/h_o$; h_m is the lubricant monolayer thickness; $\alpha = (\mu_m/\mu_o - 1)h_m/h_o$, where μ_m = 300 Pa.s for ZTMD and μ_m/μ_o = 0.3 [10]. The D(h) values for ZTMD using Eq. 4, 5 and 6 are compared in Fig. 6b and Table 1. The D(h) calculated by Eq. 6 provides a close match to the experimental D(h) reported herein and indicates that realistic values for D(h) could be accessible from knowledge of the Hamaker constant provided that a good estimate for μ_m is available. For ZTMD, setting μ_m = 300 Pa.s provided the best match between Eq. 6 and Eq. 4 as shown in Fig. 6b.

Conclusions:

The thickness-dependent diffusion coefficient as a function of ZTMD film thickness between 2 and 11 Å was determined by lubricant flow.D(h) based on the disjoining pressure gradient was similar to the experimental D(h) using a surface viscosity of 300 Pa.s for ZTMD.

Figures:

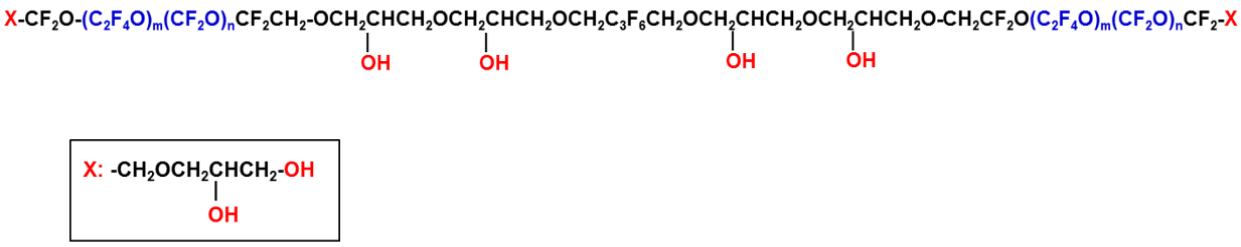

Figure 1.The chemical structure of ZTMD.

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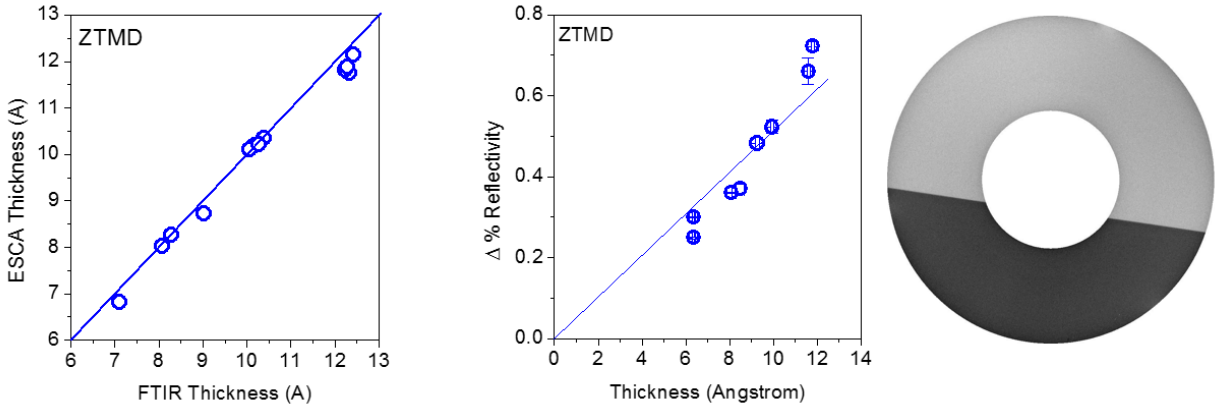

Figure 2. (Left) The ESCA-FTIR thickness calibration for ZTMD. (Right) The OSA-ZTMD reflectivity-thickness calibration for ZTMD. Half-dipped disks are used to calibrate the OSA reflectivity to the ZTMD film thickness.

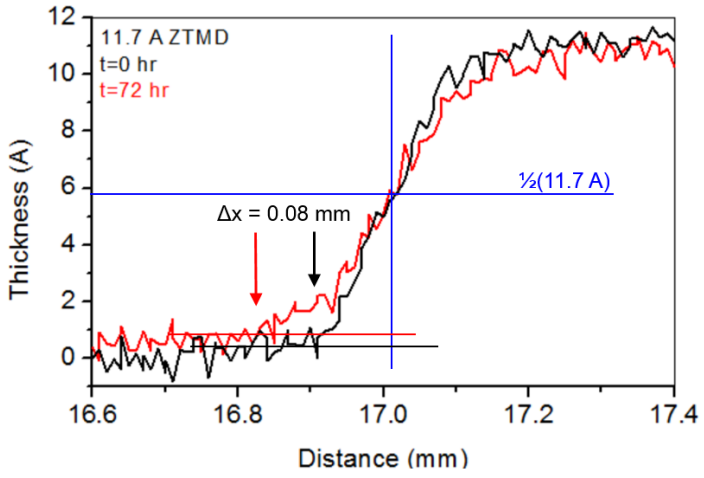

Figure 3. Methodology used to extract flow kinetics data is based on the Matano interface. Using 11.7 Å ZTMD flow as an illustrative example, the flow distance is 0.08 mm after 72 hr.

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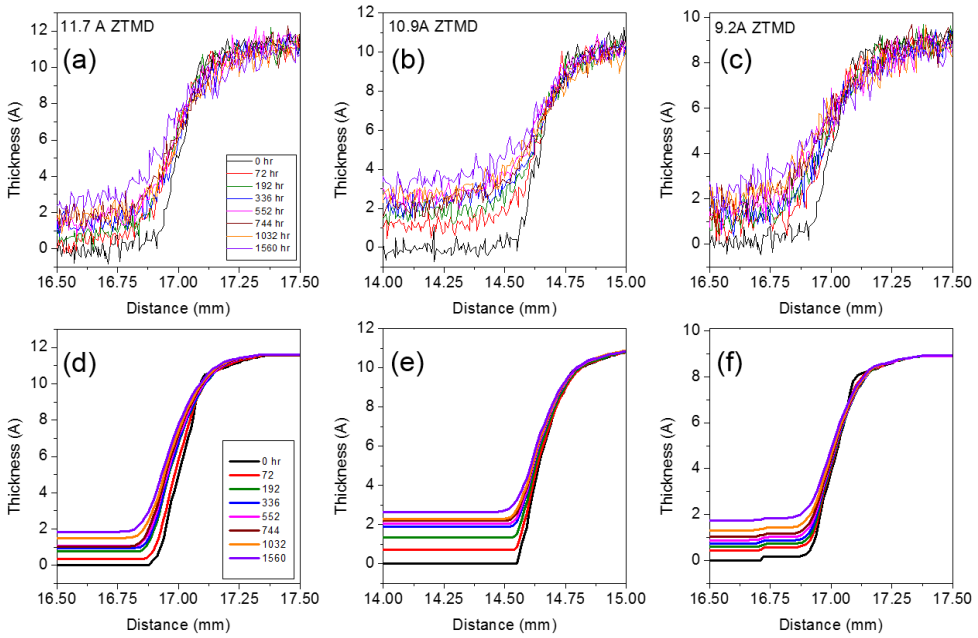

Figure 4. Experimental ZTMD flow as a function of time for (a) 11.7 Å, (b) 10.9 Å and (c) 9.2 Å. The corresponding numerical simulation for ZTMD flow as a function of time using Eq. 4 for (d) 11.7 Å, (e) 10.9 Å and (f) 9.2 Å.

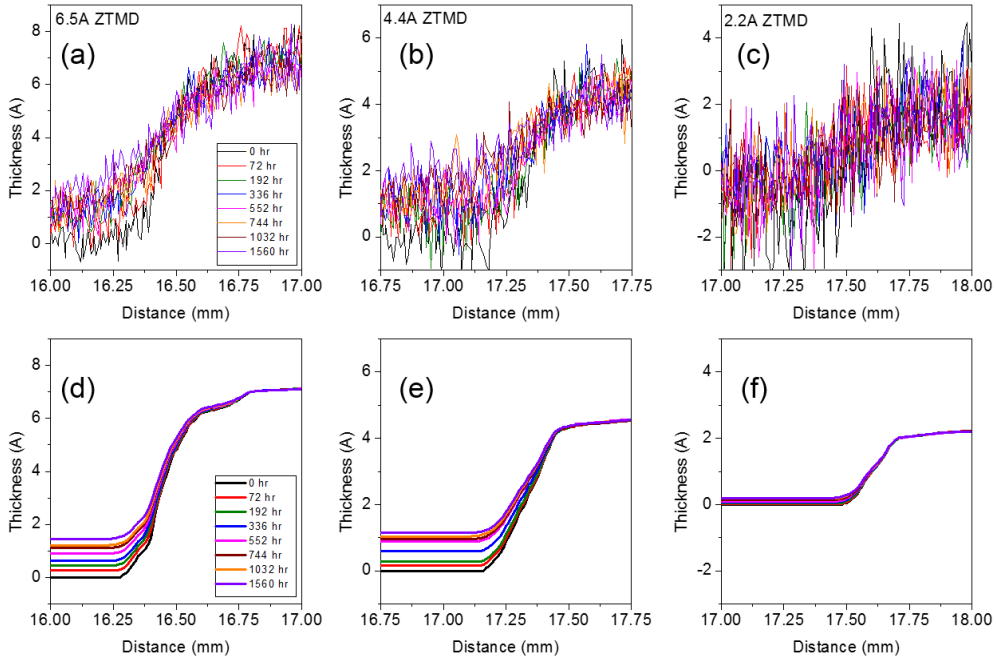

Figure 5. Experimental ZTMD flow as a function of time for (a) 6.5 Å, (b) 4.4 Å and (c) 2.2 Å. The corresponding numerical simulation for ZTMD flow as a function of time using Eq. 4 for (d) 6.5 Å, (e) 4.4 Å and (f) 2.2 Å.

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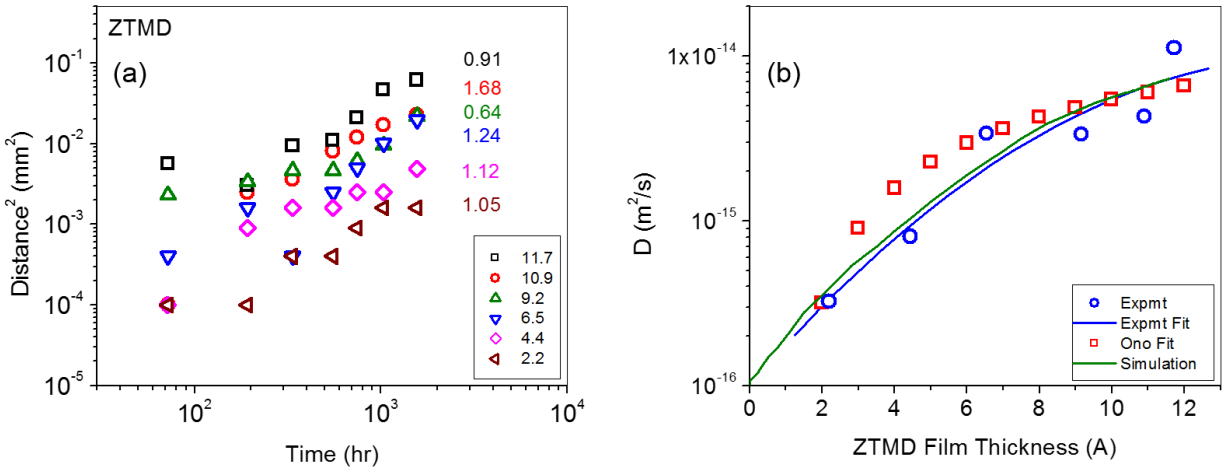

Figure 6.Experimental ZTMD flow distance versus time (Eq. 3). (b) Experimental ZTMD D(h) is compared to D(h) calculated by Eq 6. See also Table 1. The green line represents the D(h) values accessed for ZTMD during the numerical simulations for flow.

Tables:

Table 1. Comparison of D (m^2/s) values as a function of ZTMD film thickness. The d_o value is taken from [1]. The A value is taken from [4]. The viscosity is the value that provided the closest fit to the experimental data (Fig. 6b).

Thickness (Å)	Experimental This Work	Eq. 5	Eq. 6
11.72	1.12×10^{-14}	2.2×10^{-14}	0.64×10^{-14}
10.89	4.29×10^{-15}	2.3×10^{-14}	6.0×10^{-15}
9.15	3.35×10^{-15}	2.4×10^{-14}	4.9×10^{-15}
6.53	3.38×10^{-15}	2.6×10^{-14}	3.3×10^{-15}
4.44	8.04×10^{-16}	2.5×10^{-14}	1.8×10^{-15}
2.19	3.26×10^{-16}	1.6×10^{-14}	4.0×10^{-16}
Viscosity (Pa.s)		300	300
A (J)		2.8×10^{-19} J	2.8×10^{-19} J
d_o (Å)		2.0	2.0

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