Lubricant reflow for Z-Tetraol is characterized for heat-assisted magnetic recording (HAMR). The thickness-dependent diffusion constant, $D(h)$, is determined from flow experiments for submonolayer Z-Tetraol films between 2.5 and 13 Å. Fickian diffusion using experimental $D(h)$ values are used to numerically simulate lubricant reflow into HAMR laser-depleted troughs as a function of trough number, trough depth, trough distance and trough width. Reflow is computed to be slower for multiple, wider and deeper troughs. Reflow kinetics as a function of trough separation distance is complicated by adjacent trough interactions. Two major kinetic regimes are identified. Multiple troughs that have not coalesced recover more quickly. Once multiple troughs coalesce into a single larger trough, reflow kinetics is drastically slowed. The crossover time between the two kinetic regimes is computed to be approximately 400 millisec for the system under investigation here, but will be a strong function of trough number, width, depth and separation distances. The simulation of multiple troughs provides significant insight into HAMR conditions. Single trough lubricant studies may be misleading for HAMR systems.

Keywords: Z-Tetraol, hard disk drives, heat-assisted magnetic recording, reflow, diffusion

1. Introduction

Heat-assisted magnetic recording (HAMR) may supplant perpendicular magnetic recording (PMR) in the next evolution of hard-disk drives. HAMR technology utilizes an optical field to instantaneously heat the magnetic recording media and temporarily reduce its coercivity to allow magnetic recording on media of high magnetic anisotropy. The heating rate is expected to be on the order of $10^{10}-10^{11}$ K/s with a peak temperature exceeding the Curie temperature of the media, $\geq \sim 800$ K [1]. From a slider-disk interface perspective, the thermal stress is expected to challenge the robustness of today’s protective carbon and boundary lubricant films. Numerous studies have been spawned to answer the question of whether or not the current carbon and lubricant “tribological layers” can survive HAMR technology [2-11].

From strictly a boundary lubricant perspective, experimental studies have shown that laser heating removes lubricant film from the disk surface [2,8,9]. Depending upon the read-write duty cycle, the mobility of the boundary lubricant film, and the local supply of the lubricant film, reflow from the surrounding area into the thickness-depleted area may, or may not, occur at a fast enough rate to maintain tribological robustness under HAMR conditions. Many recent tribological studies indicate that lubricant coverage is the significant determinant for contamination robustness and head-disk interface reliability [12-15]. Tribological robustness must still be satisfied in the HAMR interface. Consequently, lubricant reflow into the laser-depleted area may be an important requirement of HAMR interfaces. Lubricant reflow has not been required of PMR media thus far. Several papers report on the experimental reflow kinetics following laser irradiation [2,16]. For example, approximately 24 hr was needed to recover a 12 Å Z-Tetraol trough having a 65 µm diameter [2]. In other reflow experiments, reflow kinetics into a 20 Å Zdol trough having a 1 µm diameter required ~35 millisec for 50% recovery [17]. Despite differences in the diffusion coefficients between Zdol and Z-Tetraol due to their molecular polarity [18], these data can be interpreted as smaller troughs having faster recovery rates. A recent numerical simulation of lubricant recovery after HAMR laser irradiation supports the experimental findings where smaller spots and thicker films recover faster [19].

The computer simulation of ultra-thin lubricant flow provides a powerful methodology by which lubricant
film properties required of HAMR interfaces can be understood. The conventional diffusion equation based on continuum mechanics can provide simulations that agree fairly well with experimental data if the film thickness-dependent diffusion coefficient is “parameterized” to provide the correct answer [20,21]. The thickness-dependent diffusion coefficient is either measured experimentally or obtained by modeling as a Poiselle flow driven by a disjoining pressure gradient. Experimentally derived diffusion coefficients should be the standard to which modeled diffusion coefficients are judged. In the latter case, recent improvements include corrections for submonolayer lubricant film density and a finite Hamaker constant with decreasing film thickness [22].

In this report, we investigate lubricant flow kinetics as a function of film thickness for the perfluoropolyether (PFPE) Z-Tetraol. The experimentally determined diffusion constant as a function of film thickness is then used to model lubricant reflow in HAMR applications as a function of trough size, trough density and trough spacing as might be produced by HAMR disk drives.

2. Experimental section

Z-Tetraol (2200 daltons) was purchased from Solvay-Solexis (Italy) as the GT grade (narrowly distributed) and used directly. NMR (Bruker Avance 500 MHz spectrometer) data indicates a number average molecular weight of 2050 daltons, with 93% tetraol and 7% dol adducts. The tetraol adduct refers to the -CH2OCH2CH(OH)CH2OH end group, whilst the dol adduct refers to the -CH2OH end group. The chemical structure of the main component is shown below, where \( n = 9.9 \) and \( m = 10.2 \).

\[
\text{HOCH}_2\text{CH(OH)CH}_2\text{CH(OH)CH}_2\text{O}--\text{[CF}_2\text{CF}_2\text{O}]_n--\text{[CF}_2\text{O}]_m
--\text{CF}_2\text{CH}_2\text{OCH}_2\text{CH(OH)CH}_2\text{OH}
\]

Z-Tetraol

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 PFPE lubricant films were applied to the carbon surfaces from solvent using a standard dip-coating methodology, using a typical concentration of 0.05 g/liter and a typical disk withdrawal rate of several mm/sec.

The thicknesses of the topically applied Z-Tetraol films were quantified by specular reflection FTIR (Nicolet Magna Model 560). The FTIR absorption band maximum was in turn correlated to film thickness by XPS (Phi Quantum 2000 ESCA System) using a takeoff angle of 45\(^\circ\) and an electron mean free path of 25 Å [23].
The FTIR-ESCA thickness correlation is shown in Fig. 1.

Lubricant flow as a function of time was investigated ellipsometrically using half-dipped PFPE films as shown in Fig. 2. 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 [24]. 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. The reflectivity-thickness calibration used in these studies is shown in Fig. 2.

The Z-Tetraol bonded fractions for the films used in the flow experiments are summarized in Table 1. The initial bonded fractions are measured on sister disks while the final bonded fractions are measured on the experimental disks after completion of the flow experiments. During the course of the flow experiments, the bonded fraction increases from approximately 0.4 to 0.6. The asymptotic bonded fraction for Z-Tetraol is approximately 0.8 under ambient conditions [25]. UV treated Z-Tetraol at the 0.8 bonded fraction has a constant $D$ value approximately 4 to 5 times smaller than non-UV treated Z-Tetraol [25].

![Figure 3](image)

Table 1  The bonded fraction of Z-Tetraol at the start and end of the flow experiments (Figs. 3-5).
The monolayer fraction is based on the monolayer thickness of 21 Å [25]

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Monolayer fraction</th>
<th>Bonded Fraction $t = 0$ hr</th>
<th>Bonded Fraction $t = 1149$ hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.9</td>
<td>0.61</td>
<td>0.28</td>
<td>0.45</td>
</tr>
<tr>
<td>9.7</td>
<td>0.46</td>
<td>0.30</td>
<td>0.48</td>
</tr>
<tr>
<td>7.4</td>
<td>0.35</td>
<td>0.33</td>
<td>0.54</td>
</tr>
<tr>
<td>5.1</td>
<td>0.24</td>
<td>0.39</td>
<td>0.66</td>
</tr>
<tr>
<td>2.5</td>
<td>0.12</td>
<td>0.41</td>
<td>0.68</td>
</tr>
</tbody>
</table>

![Figure 3](image)

Fig. 3  (a) Experimental 12.9 Å Z-Tetraol flow as a function of time. (b) Summary plot of the diffusion coefficient as a function of Z-Tetraol film thickness from Figs. 3(a), 4(a,b) and 5(a,b). The red line is the $D(h)$ computed and used during the numerical simulations. (c) Numerical simulation for 12.9 Å Z-Tetraol as a function of time using $D(h)$. (d) Numerical simulation for 12.9 Å Z-Tetraol as a function of time using a constant $D = 7.69 \times 10^{-13}$ m$^2$/s determined at the 12.9 Å film thickness. For (a), (c) and (d), the times corresponding to the flow profiles are: 0 (black); 71 (red); 142 (green); 263 (blue); 334 (magenta); 406 (wine); 597 (orange); 1149 hr (violet)
3. Flow simulation method

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.

\[
\frac{\partial h}{\partial t} = \frac{D}{h} \frac{\partial}{\partial x} \left( h \frac{\partial h}{\partial x} \right)
\]  

(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 [26]. In the FTCS approximation, the time step is defined for the von Neumann stability condition, Eq. 2.

\[\Delta t \leq \frac{\Delta x^2}{2D}\]  

(2)

4. Flow experimental results

Experimental flow profiles for Z-Tetraol films on CNx are shown in Figs. 3-5. Figures 3(a), 4(a,b) and 5(a,b) correspond to 12.9, 9.7, 7.4, 5.1 and 2.5 Å, respectively. The experimental data are discussed first. The diffusion process is characterized through the scaling of the mean square displacement with time using

\[x^2 \propto t^\gamma\]  

(3)

\(x\) is the distance and \(t\) is the time. When \(\gamma = 1\) normal diffusion is observed. Diffusion is anomalous for \(\gamma \neq 1\). For \(\gamma < 1\), trapping effects become dominant and subdiffusion is observed [27]. Plotting Eq. 3 as \(\log<\!x^2\!>\) versus \(\log t\) provides the experimental way to determine the type of diffusion occurring in a given system. For Z-Tetraol films between 2.5 and 12.9 Å, Fig. 6(a) indicates that \(\gamma = 0.96 \pm 0.10\) and thus lubricant flow will be treated as normal diffusion under Eq. 1. The known increase in the bonded fraction of Z-Tetraol as a function of time does not appear to significantly influence the flow kinetics (Table 1). The experimental diffusion coefficient as a function of film thickness, \(D(h)\), summarized in Table 2, is also plotted in Fig. 3(b). The polynomial fit to the experimental data points, Eq. 4, is used in all of the simulations here.

\[
D(h) = 1.02 \times 10^{-13} + (2.18 \times 10^{-11})(h) + (3.10 \times 10^{-14})(h^2)
\]  

(4)

\(h\) is the film thickness in Angstroms and \(D(h)\) is m²/s. Eq. 4 indicates that \(D(h) \rightarrow 10^{-15}\ m²/s\), not “zero”, as \(h \rightarrow 0\). As discussed later, this will cause the simulated flow to be as much as 30% larger than the experimental.
flow for the longer simulation times. The shorter simulation times appear to be well-matched and represent a significant improvement over using a constant diffusion coefficient as compared in Fig. 3(c,d). In particular, Fig. 3(d) shows the simulated lubricant flow for 12.9 Å of Z-Tetraol using the constant diffusion coefficient of 7.69 × 10^{-13} m^2/s (Table 2). Simulations using a constant diffusion coefficient exhibit the characteristic Gaussian tail that are not capable of reproducing the “molecular tongue” exhibited by interacting systems such as PFPEs with increasingly polar end groups [28].
The experimental $D(h)$ represented by Eq. 4 can be compared to other equations proposed for the calculation of submonolayer $D(h)$ based on the disjoining pressure gradient, Eqns. 5 and 6 below [20,22]. Eq. 6 differs from Eq. 5 primarily by a correction for decreasing lubricant film density with decreasing film thickness.

$$D(h) = \frac{A h^3}{6 \pi \mu (h + d_0)}$$  \hspace{1cm} (5)

$$D(h) = \frac{A}{18 \pi \mu h_m} \left( \frac{H - D_0 / 2}{H + D_0} \right)^{3/2} \left( 1 - \frac{\alpha H}{4} + \frac{\alpha_m H^2}{10} \right)$$  \hspace{1cm} (6)

$A$ is the Hamaker constant, and $\mu$ represents a surface viscosity. In Eq. 4, $h$ and $d_0$ are the film thickness and cut-off distance, respectively. In Eq. 5, $H = h / h_0$, where $h_0$ is the initial film thickness; $D_0 = d_0 / h_0$; $h_m$ is the lubricant monolayer thickness; $\alpha = (\mu_m / \mu_0 - 1) h_m / h_0$, where $\mu_m = 1$ and $\mu_m / \mu_0 = 0.3 \text{ Pa·s}$ for Z-Tetraol, respectively [22]. The $D(h)$ values for Z-Tetraol using Eqs. (4-6) are compared in Fig. 6(b). The $D(h)$ calculated by Eq. 6 provides a close match to experimental data and indicates that realistic values for $D(h)$ could be accessible from knowledge of the Hamaker constant, provided a good estimate for $\mu$ is available. Conversely, knowledge of $D(h)$ and $A$ from experiment could alternatively provide an estimate for $\mu$.

### 5. Flow simulation results

The simulated lubricant flow as a function of time in submonolayer films of Z-Tetraol 2200 are shown in Figs. 3(c), 4(c,d) and 5(c,d) for 12.9, 9.7, 7.4, 5.1 and 2.5 Å, respectively. They can be compared directly to the experimental flow curves located directly above the simulated curves since the same distance range ($x$-axis) is presented in all cases. The experimental and simulated curves generally show good agreement as discussed above. Figure 3(b) shows the actual values of the diffusion coefficient as a function of lubricant film thickness used during the simulation of the 12.9 Å simulation flow. The $D(h)$ values used in the simulation match the experimental $D(h)$ values from which they are based.

Figure 7(b) plots the reflow kinetics of a 5 mm wide Z-Tetraol trough as a function of time. This data is used to test the robustness of thickness-dependent diffusion coefficient used to describe Z-Tetraol reflow compared to using a constant diffusion coefficient. Figure 7(a) shows the reflow kinetics using a constant $D = 1.0 \times 10^{-17} \text{ m}^2/\text{s}$.
$10^{-12}$ m$^2$/s that provides the best overall fit for the shorter (< 200 hr) and longer (> 700 hr) times. A constant $D = 7.7 \times 10^{-12}$ m$^2$/s (Table 2) provides a better fit to the longer time but does not match the short time reflow. Difficulties fitting Z-Tetraol diffusional flow using a constant $D$ has also been described by Ono [22]. However, we do note that the simulation using constant $D$, Fig. 7(a), generally reproduces the experimental trough reflow, Fig. 7(b). There are two notable observations. First, the lubricant profile “roughness” observed at the bottom of the trough at $t = 0$ is quickly dissipated by using a constant $D$ value that does not decrease with decreasing film thickness. Second, reflow is predicted to be faster at longer times for the same reason. Figure 7(c) shows the reflow kinetics using the thickness-dependent diffusion coefficient. Reflow at the shorter times is much better reproduced as shown by the more gradual dissipation of the lubricant “roughness” similar to the experimental dissipation kinetics. At longer times, the reflow rate is slower than having used a constant $D$ and thus a better overall fit is achieved.

6. Flow simulation in HAMR applications

Flow simulations are next conducted for Z-Tetraol in HAMR applications using the experimentally determined $D(h)$ in Eq. 4. The HAMR laser spot size, taken as the FWHM (full width at half maximum), is expected to be approximately $40 \times 40$ nm$^2$ [29,30]. In our one dimensional simulations, we therefore choose a trough width of 50 nm as our “working model” although other trough widths will be discussed below. Thus far, most experimental HAMR laser irradiations have been conducted in the ~ 10 µm (10,000 nm) range so HAMR-realistic length scales have not yet been experimentally approached. Using Z-Tetraol as an illustrative example, we can now compute the reflow kinetics as a function of laser-induced troughs that will provide significant insight into HAMR issues that might develop for the lubricant film upon laser irradiation. As reference, we note that disks in hard disk drives spin between approximately 5000 and 10000 RPMs which correspond to 12 and 6 millisec per revolution, respectively. Lubricants that demonstrate an ability to reflow within this duty cycle time could compensate for laser-induced lubricant depletion. These aspects will be discussed in a separate presentation.

Figure 8 shows the reflow kinetics of 10 Å Z-Tetraol as a function of the number of troughs generated by HAMR laser. The simulations compare Z-Tetraol reflow as a function of the number of troughs, 1, 3, 5 and 9 limited to trough widths of 50 nm separated by 50 nm. The initial troughs are represented by square wells. The reflow rates into the troughs are plotted in Fig. 9(a) from 0 to 1 sec. The results of these simulations show that
multiple troughs slow the recovery of film thickness by reflow. For multiple troughs, the initial reflow rates are initially quite similar before they coalesce into a single larger trough, typically observed for times \( \leq \) several millisecond, under these conditions. At 10 millisecond, the troughs have coalesced to behave as a wider single trough as shown in the series Figs. 8(a-d). Conclusions based on single-spot reflow kinetics will therefore be misleading in HAMR lubricant studies. As a check on the simulations, Fig. 9(b) plots the \( D(h) \) as a function of Z-Tetraol film thickness actually used during the simulation shown in Fig. 8(a). As expected, \( D(h) \) matches Fig. 3(b).

Figure 10 shows the reflow kinetics of 10 Å Z-Tetraol as a function of the trough depth for 2, 4, 6 and 8 Å depths. Simulations using 5 troughs of 50 nm widths and

![Graph](image1)

**Fig. 9** (a) Summary plot from Fig. 8 for the numerical simulation of 10 Å Z-Tetraol reflow as a function of time from 0 to 1 sec and of the number of troughs. (b) Summary plot of \( D(h) \) computed and used during the numerical simulations. This plot verifies \( D(h) \) matches the experimental \( D(h) \) shown previously in Fig. 3(b) for all trough simulations conducted in Figs. 8-12.

![Graph](image2)

**Fig. 10** Numerical simulation for 10 Å Z-Tetraol reflow as a function of time and of trough depth for (a) 2; (b) 4; (c) 6; and (d) 8 Å trough depths. All simulations are conducted on 5 troughs that are initially 50 nm wide and are separated by 50 nm between adjacent edges (or 100 nm between trough centers). The 10 Å trough depth was previously shown in Fig. 8(c). The reflow kinetics are based on \( D(h) \) using Eq. (4).
50 nm separation distances are considered here. The initial troughs are represented by square wells. The corresponding 10 Å trough was already considered in Fig. 8(c). The reflow rates as a function of trough depth are plotted in Fig. 11 from 0 to 1 sec. The simulations indicate that deeper troughs slow the recovery of film thickness by reflow.

Figure 12 shows the reflow kinetics of 10 Å Z-Tetraol as a function of the trough separation distances of 25, 100 and 150 nm. The trough depth and width are fixed at 10 Å and 50 nm, respectively. The initial troughs are represented by square wells. The reflow rates into the troughs separated by edge-to-edge distances between 25 and 200 nm are plotted in Fig. 11(b) from 0 to 1 sec. These simulations indicate that adjacent trough interactions are a significant determinant of reflow kinetics. In particular, multiple troughs that are separated by larger distances recover more quickly initially because they are isolated for a longer period of time. However, once the troughs coalesce at longer times, the reflow rates decrease significantly. The crossover between these two kinetic regimes occurs at about 400 millisecond under these conditions. Thus, larger trough separations are indicated for better reflow healing.

Figure 13(a-c) shows the reflow kinetics of 10 Å Z-Tetraol as a function of the trough width for 50, 30 and 10 nm wide troughs. Simulations using 5 troughs of 10 nm edge-to-edge separation distances are considered here. The initial troughs are represented by square wells. The reflow rates as a function of trough width are plotted in Fig. 13(d) from 0 to 1 sec. The simulations indicate that wider troughs slow the recovery of film thickness by reflow.

7. Conclusions

The diffusion coefficient as a function of film thickness for Z-Tetraol was determined experimentally between 2.5 and 13 Å. The $D(h)$ values were then used to simulate lubricant reflow under HAMR conditions. Reflow rates as a function of trough number (1, 3, 5 and 9), trough depth (2, 4, 6, 8 and 10 Å), trough separation
distances (25, 50, 100, 150 and 200 nm), and trough width (10, 30, 50 nm) were simulated numerically using Fickian diffusion with the experimentally derived thickness-dependent diffusion coefficient. Reflow was computed to be slower for multiple, wider and deeper troughs. Reflow kinetics into multiple troughs showed two kinetic regimes. Isolated multiple troughs showed a relatively faster reflow kinetics. When the multiple troughs coalesced into a single, larger trough, reflow kinetics slowed dramatically thereby reducing trough recovery. Reflow simulations into multiple troughs provided significant insight into HAMR conditions. Conclusions based upon single trough studies are identified to be possibly misleading for HAMR systems.

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