

RELAXATION OF A SURFACE SCRATCH

BY VISCOUS FLOW

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ABSTRACT

The Fourier - Moment method developed by King and Mullins has been applied to the case of an isolated scratch decaying by viscous flow in an amorphous material such as a simple glass. Using the Stokes-Einstein equation to relate the diffusivity and viscosity coefficients, a comparison of rates suggests that viscous flow would predominate over volume or surface diffusion as the mechanism of scratch healing in simple amorphous materials for scratch widths above approximately 0.1 microns.

INTRODUCTION

The smoothing of an isolated scratch on the surface of a heated solid represents one of several capillarity-induced phenomena in which forces of surface tension motivate changes in topography. Over the last few years a number of publications have appeared in the literature describing the kinetics of decay of single and multiple scratches by surface diffusion, volume diffusion, and evaporation - condensation¹⁻⁵. While diffusional mechanisms are thought to contribute significantly to scratch healing in crystalline bodies, another type of mechanism, namely, viscous flow may be important in non-crystalline glasses and organic polymers. Powders of these substances appear to sinter by a viscous flow rather than a diffusional mechanism⁶. The purpose of this communication is to extend the theory of scratch smoothing to include smoothing by a mechanism of viscous flow*.

FOURIER INTEGRAL FORMULATION AND SOLUTION FOR AN ISOLATED SCRATCH DECAYING BY VISCOUS FLOW

Consider an isolated scratch whose profile lies in the XZ-plane as illustrated in Figure 1. Following King and Mullins², the scratch can be represented, mathematically, as a Fourier integral in the

*The authors have recently become aware that Dr. N.A. Gjostein of the Ford Scientific Laboratory has independently derived results similar to those reported here⁷.

form

$$z_{VF}(x, t) = \int_{-\infty}^{+\infty} f_0(\omega) e^{-\xi(\omega)t} \cdot e^{i\omega x} d\omega \quad (1)$$

where

$$f_0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} z(s, 0) e^{-i\omega s} ds \quad (2)$$

$\xi(\omega) = \gamma\omega/2\eta$ is the decay factor for viscous flow (VF), $\omega = 2\pi/\lambda$ is the frequency of a Fourier component, γ is the surface tension and η the viscosity coefficient. s is a dummy variable of integration equivalent to x . King and Mullins² have solved Eq.(1) for the surface and volume diffusion cases. Since the mathematical procedure is the same in the case of viscous flow we shall simply give the solution and refer the reader not familiar with the details to their paper.

$$z_{VF}(x, t') = \frac{\langle x' \rangle_0}{\pi (Ft')^2} \int_0^{\infty} k e^{-k} \sin(u_{VF} k) dk - \frac{\langle x'^2 \rangle_0}{2\pi (Ft')^3} \int_0^{\infty} k^2 e^{-k} \cos(u_{VF} k) dk \quad (3)$$

where $F = \gamma/2\eta$, a new variable of integration k defined by $\omega \equiv k/F t'$ has been introduced, and $u_{VF} = X/Ft'$ is a reduced length. The time t' appearing in Eq. (3) is the sum of the experimental running time t

and an additive constant t_0 as discussed by King and Mullins. It is seen from Eq. (3) that the shape of the profile remains unchanged during the flattening process, since the shape is reflected by the weighting factors $\langle X^n \rangle_0$ which occur outside the integrals. The quantities appearing under the integral signs reflect only the decay process - in this instance, viscous flow.

The integrals in Eq. (3) are standard and can be readily evaluated. Employing a notation used by Gruber and Mullins⁴, we define a "scratch strength" α_{VF} by $\alpha_{VF} \equiv \langle X^2 \rangle_0 / 2(Ft')^3$ and the "degree of asymmetry" ρ_{VF} as $\rho_{VF} \equiv 2\langle X^1 \rangle_0 (Ft') / \langle X^2 \rangle_0$. In terms of these parameters the scratch profile becomes

$$Z_{VF}(x, t') = \alpha_{VF} \left[\rho_{VF} f_{VF1}(u_{VF}) - f_{VF2}(u_{VF}) \right] \quad (4)$$

where

$$f_{VF1}(u_{VF}) = \frac{1}{\pi} \int_0^{\infty} k e^{-k} \sin(u_{VF} k) dk = \frac{2 u_{VF}}{\pi (1 + u_{VF}^2)^2} \quad (5)$$

and

$$f_{VF2}(u_{VF}) = \frac{1}{\pi} \int_0^{\infty} k^2 e^{-k} \cos(u_{VF} k) dk = \frac{2(1 - 3u_{VF}^2)}{\pi (1 + u_{VF}^2)^3} \quad (6)$$

It will be observed from Eq. (4) that, as in the cases of surface and volume diffusion previously analyzed⁴, the amplitude of the scratch

profile is reflected by the magnitude of the scratch strength, whereas the degree of asymmetry determines its shape. For an isolated scratch decaying to flatness by viscous flow the amplitude decreases with time as $1/t'^3$. However, the anti-symmetric component increases linearly with time.

For purposes of plotting Eq. (4) has been rewritten in the standard form

$$\frac{z_{VF}(X, t')}{\beta} = \rho_{VF} \left[\frac{u_{VF}}{(1+u_{VF}^2)^2} \right] - \left[\frac{1-3u_{VF}^2}{(1+u_{VF}^2)^3} \right] \quad (7)$$

where we have let $1/\beta = \pi/2\alpha_{VF}$ and have substituted expressions (5) and (6). Figure 2 shows typical scratch profiles obtained from Eq. (7) for four different values of the degree of asymmetry. The strong dependence of the shape of the scratch on ρ_{VF} is clearly evident. The profile corresponding to $\rho_{VF} = 0$ is the standard symmetric profile for a scratch decaying by viscous flow. An interesting feature of the profiles is that they do not exhibit an indefinite number of oscillations that seems to be a characteristic of scratches healing by a diffusional mechanism^{2,4}. The behavior displayed here is quite similar to that predicted by Mullins⁹ in the late stages of the sintering of a wire to a plane surface by viscous flow.

DISCUSSION

It is of particular interest to compare the rates of the various mass transport processes that can play a role in the smoothing of a

scratch. A useful parameter in making such a comparison is the scratch width W , defined simply as the separation distance between maxima in the scratch profile. For the case of a symmetric scratch the pertinent relationships are summarized below:

$$\begin{aligned} W &= 2Ft' && \text{for viscous flow (this work)} \\ W &= 6.22(Dt')^{1/3} && \text{for volume diffusion (King-Mullins} \\ &&& \text{Ref. 2)} \\ W &= 6.90(Bt')^{1/4} && \text{for surface diffusion (King-Mullins} \\ &&& \text{Ref. 2)} \end{aligned}$$

where $D = D_V \gamma_S \Omega_0 / KT$ and $B = \gamma_S D_S \Omega_0^2 / KT$ are material parameters defined by King and Mullins². Since we are interested in comparing rates, it is necessary to form expressions for the relative time rate of increase of W . Denoting the time derivative of W by \dot{W} one obtains

$$\frac{\dot{W}_{VF}}{\dot{W}_V} = \frac{6}{(6.22)^3} \cdot \frac{F}{D} W^2 \quad (8a)$$

$$\text{and } \frac{\dot{W}_{VF}}{\dot{W}_S} = \frac{B}{(6.90)^4} \cdot \frac{F}{B} W^3 \quad (8b)$$

$$\frac{F}{D} = \frac{kT}{2\eta D_V \Omega_0} \text{ cm}^{-2}, \quad \frac{F}{B} = \frac{kT}{2\eta D_S \Omega_0^{4/3}} \text{ cm}^{-3}$$

where the subscripts VF, and V and S refer to viscous flow, volume diffusion and surface diffusion, respectively. Ω_0 is the volume occupied by a molecule. From Eq.(8a) it is evident that if $W < \left[\frac{(6.22)^3}{6} \cdot \frac{D}{F} \right]^{1/2}$ volume diffusion will be the preferred mechanism of scratch healing

compared to viscous flow, while from Eq.(8b) surface diffusion will be more important than viscous flow when the scratch width is less than

$$\left[\frac{(6.90)^4}{8} \cdot \frac{B}{\bar{r}} \right]^{1/3} \text{ cm}^* .$$

While the exact nature of the relationship between the diffusivity and viscosity is not known for all substances, it appears that the diffusivity and viscosity of solids at elevated temperatures are related quantities. For example, Turnbull and Cohen¹⁰ believe it possible, although not proven, that an equation having the form of the Stokes-Einstein relation $D_V = bT\phi$ holds for glasses over the entire fluidity range. For simple liquids the parameter b is usually close to the Stokes-Einstein value, $b = \frac{k}{3\pi\alpha_0}$ so that $D_V = \frac{kT}{3\pi\alpha_0} \phi$, the quantity ϕ being equal to the reciprocal of the viscosity coefficient η and α_0 is the molecular diameter. If the Stokes-Einstein equation is taken as a limiting case to express the relationship between the diffusivity and viscosity of an amorphous substance then, assuming $\alpha_0 \approx 10^{-7}$ cm, it appears from Eq.(8a) that viscous flow would be a more rapid scratch healing process than volume diffusion for scratch widths in excess of about 20Å. Assuming further that $D_S \sim 10^4 D_V$ it can be calculated from Eq.(8b) that viscous flow would also predominate over surface diffusion when the scratch width exceeds approximately 0.1 microns. Viscous flow, therefore, may play a far more important role in the healing of scratches in amorphous

*This conclusion may also be inferred from Mullins' paper (Reference 9) if the wavelength λ of the sinusoidal perturbations which he considered is replaced by the scratch width W .

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substances than it does in crystalline substances where it seems quite likely that diffusion mechanisms predominate.

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