Smoothing Effects of Surface Tension on Grooved Melt Wires

by

B. J. Thamer
SMOOTHING EFFECTS OF SURFACE TENSION ON GROOVED MELT WIRES

by

B. J. Thamer

ABSTRACT

Possible interference of scratch smoothing in detecting melting of cylindrical, grooved melt wires has been investigated theoretically and experimentally. Isotropy has been assumed for surface tension and diffusion coefficients. The rate of diagonal build-up of material in the bottom corner of the groove below the melting point has been calculated from known transport processes. The higher-order terms omitted in Mullins' original treatment of scratch smoothing have been retained in solving the differential equation by the method of finite differences. Other methods of solution also are discussed. The time required to give objectionable build-up (> 1 mil) is calculated to be 2 days for vacuum-sealed zinc, 3 months for vacuum-sealed silver, 8 months for copper encased in graphite, 4 yr for nickel in graphite, and 5 months for platinum in graphite. The calculation is supported by experimental observations for silver. In the absence of appreciable vapor transport, the smoothing is generally determined by Mullins' $C = \gamma \Omega D_v / kT$, where $D_v$ is by a vacancy mechanism. At the normal melting point, the surface tension of a pure metal is generally proportional to the melting temperature and $C = 10^{-15}$ cm$^3$/sec if $D_v$ is by vacancies. From this the smoothing of nonvolatile, unalloyed melt wires should be innocuous for at least 1 month.

I. Introduction

Encased melt wires have been used for the remote measurement of temperature in the UHTREX reactor at the Los Alamos Scientific Laboratory (LASL). The indication of melting has been observed under a microscope in a circumferential groove of square outline that has been machined in a cylindrical wire of the chosen material. A false indication of melting is also possible if the smoothing effects described by Mullins and others are large enough in the solid state. The latter effects are due to capillarity and require an appreciable time to occur in contrast to the instanty of melting. The interference is estimated for some melt-wire materials for which relevant data are available. Isotropy is assumed for surface tension and diffusion coefficients. A more refined treatment is usually not justified by the available data.

Figure 1 depicts the outline of the machined groove located half way along the 1/4-in. length of the melt wire. The principal interference of the smoothing effects is at the bottom corner of the groove where melting would first appear. At that location ($x = 0$), transport processes initially build up material at an approximately $45^\circ$ angle to the wall. The early stages and short-range transport of the process may be derived in terms of the two solid-lined walls $c$ and $c$ of Fig. 1. It is unnecessary to assume a single sine wave to represent the initial geometry as was done by Blakely and Mykura. Their approach, and the more general one of King and Mullins, are based upon Mullins' equations that will be discussed later. As in previous treatments, it is necessary to represent the initial profile by a Fourier equation.

$$y_{in} = \frac{c}{2^{3/2}} \left[ 1 - \frac{8}{\pi^2} \sum_{\text{odd } n} \frac{1}{n^2} \cos \left( \frac{2\sqrt{2} \pi n x}{c} \right) \right]. \quad (1)$$

It is readily verified that $y_{in} = 0$ at $x = 0$ by the mathematical equality.


\[
\cos\left[2^{\frac{1}{2}}\pi x/c\right] + 3^{-2}\cos\left[3\left(2^{\frac{1}{2}}\pi x/c\right)\right] + 5^{-2}\cos\left[5\left(2^{\frac{1}{2}}\pi x/c\right)\right] + \ldots = \left(\pi^2/4c\right)(c/2 - 2^{\frac{1}{2}}x) = \pi^2/8.
\]

Equation (1) contains the lines c-c of Fig. 1 as a unit in a series of infinite sawteeth for which Eq. (1) is rigorously correct. This model of the groove is therefore unrealistic beyond the distance c from the origin in the x-y plane. Nevertheless, it should suffice at the location of interest \(x = 0\), and for times that are short enough for material transport over distances less than c. The validity of this assumption will be discussed later in noting the effects on the calculations of changing the parameter c, thus indicating whether or not deficiencies of the model a distance c from the origin are important in the early stages.

The initial value of y of Eq. (1) is composed of a zeroth-order term \(c/2\) and the cosine terms \(- (2^{3/2} c/\pi^2 n^2)\cos(2^{\frac{1}{2}}\pi nx/c)\), that is, \(y_{00}\). All of these terms represent surfaces of revolution and undergo rates of smoothing, \(\partial y_{00}/\partial t\) and \(\partial y_{n}/\partial t\), that are proportional to the curvatures and surface tension. Equation (2) is the Gibbs-Thomson relation that governs the smoothing for each Fourier component. It has been derived for three dimensions by Herring.\(^{10}\)

\[
\mu = \Omega \gamma (K_{xy} + K_{ cyl}).
\]  

(2)

where \(\mu\) is the chemical potential per atom in excess of that for a flat surface, \(\Omega\) is the atomic volume, \(\gamma\) is the surface tension of the solid, and \(K_{xy}\) and \(K_{cyl}\) are the principal curvatures. The curvature \(K_{xy}\) in the x-y plane is defined by

\[
K_{xy} = -y_n''/(1 + y_n'^2)^{3/2}.
\]

As smoothing progresses, \(y_n\) retains the frequency \(\omega = 2^{\frac{1}{2}}\pi nx/c\) but changes in amplitude, thus giving for \(y_n\)

\[
K_n = K_{xy} + K_{cyl} = +c\omega^2 y_n/(1 + y_n'^2)^{3/2}
\]  

\[
+ (1 - y_n')/(2^{\frac{1}{2}}k + x + y_n)(1 + y_n'^2)^{3/2}.
\]  

(3)

Equation (3) and the differential equations to follow will also suffice for \(y_0\) if one takes \(\omega = 0\), \(y_n' = 0\), and \(y_n'' = 0\).

It will be assumed that the slope \(y_n^*\) is small with respect to unity for each significant Fourier component at the point of interest, \(x = 0\). However, there will not be as much reliance on this assumption as in some of Mullins' publications.\(^{2,4,6}\) The assumption is initially satisfied by \(y_n^* = 0\) and is approximately satisfied for a considerable length of time. Hence, the mathematical time should be identified with the experimental time rather than with a fictitious one during at least the early stages of the smoothing. The present small-slope approximations are better than they would have been if the x-y axes had been rotated 45° to the right where larger values of \(y_n^*\) would have resulted near x = 0.

Of the various modes of material transport described by Mullins,\(^{2,3}\) that due to viscous flow may be ignored here because the melt wires are crystalline.\(^{12}\) The other means of transport are evaporation-condensation to be considered in a closed system with long or short mean free path of the vapor, volume diffusion in the solid, and surface diffusion. The contribution of each of the latter effects to \(\partial y_n/\partial t\) is derived briefly for the present geometry partly to show some significant differences from Mullins' results whose derivations are followed in the main.\(^{2,3,5}\) Except for \(y_0\), each \(y_n\) is initially negative and the contribution of each smoothing effect to \(\partial y_n/\partial t\) must be positive to give the expected damping effect in the early stages. After \(y_n\) and \(y_0\) are obtained as a function of time for \(x = 0\), Eq. (4) is used to calculate \(\Delta y = y_{00}\) because \(y_{00} = 0\).

\[
y = y_0 + \sum_{Odd n} y_n.
\]  

(4)

The summation is preferred rather than integration partly because of better accuracy and partly because the series
II. Derivation of the Applicable Equations

For phenomena of evaporation-condensation, Eq. (2) becomes

\[ \ln(p/p_0) = \Omega \gamma(K_{xy} + K_{cy1})/kT = \Delta p/p_0, \]  

(5)

where \( p_0 \) and \( p \) are the metal's vapor pressure over its flat surface and surface of curvature \( (K_{xy} + K_{cy1}) \), respectively. If the vapor has a mean free path much greater than \( c/2\gamma n \) (case \( E_1 \)), one may write \( \theta = p/(2\pi nkT)^{1/2} \), where \( \theta \) is the number of atoms emitted/second-square centimeter, \( n \) is the weight of a molecule of the solid's vapor, and the coefficient of evaporation is taken to be unity.\(^{1,11}\) We therefore obtain

\[ \theta - \theta_0 = \Delta p/(2\pi nkT)^{1/2} \]

(6)

Multiplying the latter by \(-\Omega\), one obtains the rate of growth along the normal at the curvature \( (K_{xy} + K_{cy1}) \).

\[ (\partial y_n/\partial t)/(1 + y_n^{1/2})^{3/2} = -A (K_{xy} + K_{cy1}) \]

(7)

where

\[ A = p_0 \Omega \gamma^2/(2\pi nkT)^{3/2} \]

The substitution of Eq. (3) with \( x = 0 \) and \( y_n = 0 \) gives the following for mechanism \( E_1 \).

\[ (\partial y_n/\partial t)_{E_1} = -A [(\omega^2 y_n + 1/(2\frac{x}{2} k + y_n)] \]

(10)

Hence, one predicts from the model that, if \( E_1 \) is the only operative mechanism, a component \( y_n \) (not \( y_0 \)) will not decay to zero as would be the case for the groove embedded in a plane \( (k = \infty) \), but rather \( y_n \) will approach \( -k \omega + (k^2 \omega^2 - 2)^{1/2}/(2\pi \omega) y_n_{0,0} \) due to the effect of cylindricality. The prediction in this extreme should hold best when the model is simultaneously most valid, for example, for \( n > 1 \) with the present model. It is implicit in Eq. (6) that the vapor is in equilibrium with surfaces of zero curvature. This condition is not always perfectly met, as shown in Sec. IV. Otherwise, Eq. (6) is applicable, with little error, to the present melt wire of zinc vacuum-sealed in quartz.

Alternatively, if the mean free path is much shorter than \( c/2\gamma n \), then the vapor transport is by gaseous diffusion (case \( E_2 \)) assuming the absence of thermal convection. Vapor transport by \( E_2 \), though small, is operative with those of the melt wires, described in this report, that are encased in graphite under 500 psi of helium. Because the vapor density is proportional to the vapor pressure, Eq. (5) becomes

\[ \rho_s = \rho_0 + \rho_0 \Omega \gamma(K_{xy} + K_{cy1})/kT, \]

(11)

where \( \rho_s \) and \( \rho_0 \) are the vapor densities \((\text{molecules/cm}^3)\) adjacent to the surface at curvatures \( (K_{xy} + K_{cy1}) \) and zero, respectively. The diffusion is quasi-steady-state in the closed system and Laplace’s equation applies in the form \( T^2 \rho = 0 \), where the cylindrical coordinates of Fig. 1 are used in the gas phase. The term containing \( \partial^2 \rho/\partial \theta^2 \) is zero because of cylindrical symmetry. The term \( \partial^2 \rho/\partial \theta^2 \) may be obtained at the surface from Eqs. (3) and (7) with the aid of the coordinate relations \( X = x/2^{1/2} - y/2^{1/2} \) and \( Y = k + x/2^{1/2} + y/2^{1/2} \). Laplace's equation is solved with \( \rho_s \) specified by Eq. (7) and \( \rho = \rho_0 \) for \( Y \rightarrow \infty \). The solution is

\[ \rho = \rho_0 + (\rho_0 \Omega \gamma/kT)K_n K_0(\alpha_1)/K_0(\alpha_2), \]

(12)

where \( K_0(\alpha) \) and \( K_0(\alpha_1) \) are zero-order, modified Bessel functions of the second kind,

\[ \lambda = 2^{1/2} (\lambda/K_n)^{1/2}, \]

(13)

\[ \alpha = \alpha_1 = \alpha \quad \text{for} \quad Y = k + y_n/2^{1/2}. \]

The build-up of metal in the \( Y \) direction for each Fourier component is

\[ \left( \partial y_n/\partial t \right)_{E_2} = + A' \left[ J_1(\alpha_1)/J_0(\alpha_1) \right] \lambda K_n^{1/2} \]

(14)

for \( \lambda > 0 \) and \( K_n > 0 \),

where \( J_1(\alpha_1) \) and \( J_0(\alpha_1) \) are Bessel functions of the first kind, and

\[ \left( \partial y_n/\partial t \right)_{E_2} = - A' \left[ J_1(\alpha)/J_0(\alpha) \right] \lambda K_n^{1/2} \]

(15)

for \( \lambda > 0 \) and \( K_n > 0 \).
The region \( \lambda < 0 \) and \( K_n > 0 \) is appropriate for \( y_n \) for which \( \alpha_n = \sqrt{2} \). In the case of the groove in a plane, Eq. (12) applies with \( k = \infty, \alpha_n = \infty, \) and \( K_1(\alpha_n)/K_n(\alpha_n) = 1 \). Then, taking a minus sign at the square root, one obtains the following from Eq. (12).

\[
\frac{\partial y_n}{\partial t}_{E_2, p_1} = -A\omega^2y_n(1 + 3\omega^2y_n^2)^{1/2}
\]  

(16)

Equation (16) is not restricted to a square groove, of course. Mullins' result \(^5\) differs from Eq. (16) not having the term \((1 + 3\omega^2y_n^2)^{1/2}\). The difference is not negligible in this work although initial assumptions made it so in Mullins' paper. Returning to Eq. (12), one notes that if case \( E_2 \) is the only operative mechanism for a melt wire, then (as with case \( E_1 \)) a component \( y_n \) should not decay below about one-eighth of its initial value.

In assessing the effect of volume diffusion in the solid, it is important to remember that the diffusion coefficient \( D_v \) must refer to diffusion by a vacancy mechanism in the present problem.\(^6\) This identification is assumed to be valid for the experimental diffusion coefficients of metals that are face-centered cubic. The requirement is thus met for all of the present metals, assumed to be valid for the experimental diffusion coefficient \( D_s \) is the coefficient of surface diffusion, and \( v \) is the number of diffusing atoms per unit area. It is applicable to a surface of revolution. The quantity \((\partial y_n/\partial t)_s\) may be evaluated from

\[
(\partial y_n/\partial t)_s = (B/Y)(\partial/\partial s)(Y\partial K_n/\partial s)
\]

for the effect of surface diffusion, where \( B = D_s\gamma\Omega^2\nu/kT \). \( D_s \) is the coefficient of surface diffusion, and \( \nu \) is the number of diffusing atoms per unit area. In the case of the groove in a plane, Eq. (16) is not restricted to a square groove, of course. Mullins' result \(^3\) differs from Eq. (16) not having the term \((1 + 3\omega^2y_n^2)^{1/2}\). The difference is not negligible in this work although initial assumptions made it so in Mullins' paper. Returning to Eq. (12), one notes that if case \( E_2 \) is the only operative mechanism for a melt wire, then (as with case \( E_1 \)) a component \( y_n \) should not decay below about one-eighth of its initial value.

The foregoing processes may act simultaneously except that either \( E_1 \) or \( E_2 \) is to be eliminated because they are mutually exclusive.

\[
\frac{\partial y_n}{\partial t} = [(\partial y_n/\partial t)_{E_1} \quad \text{or} \quad (\partial y_n/\partial t)_{E_2}]
\]

(23)

Mechanism \( E_1 \) is given by Eq. (6), \( E_2 \) is given by Eqs. (12) through (15), volume diffusion in the solid is given by Eqs. (17) through (19), and surface diffusion is given by Eq. (21). If surface diffusion is absent, then Eqs. (10) and (11) will always have \( \lambda < 0 \) and \( K_n < 0 \) in the present geometry so that the appropriate equations for \( y_n \) will be Eq. (12) for \( E_2 \) and Eq. (17) for volume diffusion in the solid. The analog of Eq. (23) for \( y_o \) is

\[
y_o = \begin{cases} 
A(2^{1/2}k + y_0)^4 & \text{or} \quad -2^{1/2}A(2^{1/2}k + y_0)^2J_1(\sqrt{2})/J_0(\sqrt{2}) \\
+2^{1/2}C(2^{1/2}k + y_0)^2J_1(\sqrt{2})/J_0(\sqrt{2}) + B(2^{1/2}k + y_0)^3 & \text{or} \quad 2^{1/2}C(2^{1/2}k + y_0)^2J_1(\sqrt{2})/J_0(\sqrt{2}) \end{cases}
\]

(24)

Equations (23) and (24) are best handled by computer. However, some comparatively simple solutions are possible in restricted cases. For example, if the groove is
in a plane, then \( y_o \) remains \( 2^{-3/2} \). If, further, only volume diffusion is operative \( (A = B = 0) \), then Eq. (23) reduces to the sum of Eqs. (16) and (20). Equation (4) then yields the solution

\[
y_{pl,v} = \frac{c}{2^{3/2}} \left\{ 1 - \frac{8}{\pi^2} \sum_{n \text{ Odd}} \frac{n^2 \cosh[(A' + C)\omega^3 t]}{n^2 + \frac{48}{\pi^2} \sinh[(A' + C)\omega^3 t]} \right\}.
\]

(25)

where \( \omega = 2^{1/2} \pi n/c \) as usual. Equation (25) may be used to a good approximation with the existing data for platinum because \( A = A' = 0 \) and \( 2^{1/2} \pi B/cC \approx 10^{-2} \). An analogous solution with the approximation \( 1 + 3\omega^2 y_n^2 \approx 1 \) in Eqs. (16), (20), and (22) is to be found as the case \( A = A' = 0 \) in

\[
y_{pl,v} \approx \frac{c}{2^{3/2}} \left\{ 1 - \frac{8}{\pi^2} \sum_{n \text{ Odd}} \frac{n^2 \exp(-[A\omega^2 + (A' + C)\omega^3 + B\omega^4]t)}{n^2 + \frac{48}{\pi^2} \exp(-2B\omega^4 t)} \right\}.
\]

(26)

Equation (26) has the advantage of including all smoothing effects. Most of the summing for Eq. (26) can be replaced by integration as shown in the Appendix [Eq. (31)] if one smoothing effect dominates. Figure 2 shows the calculated curves for graphite-encased platinum according to Eqs. (25), (26), and (31) in the planar case, and according to Eqs. (23) and (24) with the present solution to Eqs. (23), (24), and (4) for only surface diffusion for the groove in a plane is as follows.

\[
y_{pl,s} = \frac{c}{2^{3/2}} \left\{ 1 - \frac{8}{\pi^2} \sum_{n \text{ Odd}} \frac{\exp(-B\omega^4 t)}{n^2 + \frac{48}{\pi^2} \exp(-2B\omega^4 t)} \right\}.
\]

The latter equation might be applicable considerably below the normal melting point of the metal, for example.

The method of finite differences was generally used to solve Eqs. (23) and (24) over the desired range of time. A fourth-order Runge-Kutta method was used. The chosen program estimated the truncation error and adjusted the size of integration step to keep the error below an assigned level. This feature was necessary because the equations for some of the higher Fourier components were difficult to integrate without it. The values of \( y \) were then readily obtained by Eq. (4).

III. Calculated Solutions

Sufficient data for the present calculations have been found in the literature for five of the compositions used in the melt wires for UHTREX (Table I). The coefficient of surface diffusion is assumed to be negligible for zinc because usually \( 2^{1/2} \pi B/cC < 1 \) at the melting point and, for this metal, \( 2^{1/2} \pi C/cA < 1 \), that is, the effect of vapor pressure predominates in these melt wires, which are vacuum-sealed in quartz as are those of silver. The last three metals are encased in graphite (-/C). The effects on transport of dissolved carbon are ignored for these metals because its effects are unknown and its solubility is small, being greatest \( 2.7 \) at. % in nickel. The atomic volume \( \Omega \) is corrected for volumetric expansion for every case in this report.

The results of the finite-difference method with Eqs. (23), (24), and (4) are plotted in Fig. 3 except for Pt/C which has already appeared in Fig. 2. When surface diffusion was assumed to be absent, as with zinc, each value of \( y_n \) moved toward, and eventually stopped at, \( \sim y_n,o/8 \). When \( y_n \) for Ag, Cu/C, Ni/C, and Pt/C reached \( \sim y_n,o/8 \), it continued to move sluggishly in the range between \( \sim y_n,o/8 \) and zero. The latter behavior was to be expected from the sum of Eqs. (18) and (21) because Eq. (18) can be either positive or negative, and volume and
TABLE I
DATA FOR THE CALCULATION OF A, A', C, AND B

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temp (°C)</th>
<th>γ (dyne/cm)</th>
<th>( p_0(A_2) )</th>
<th>( D_s(\text{cm}^2/\text{sec}) )</th>
<th>( D_c(\text{cm}^2/\text{sec}) )</th>
<th>( D_l(\text{cm}^2/\text{sec}) )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>420</td>
<td>717</td>
<td>1.92 \times 10^{-4}</td>
<td>1.06 \times 10^{-8}</td>
<td>--</td>
<td>(Zero)</td>
<td>16-19</td>
</tr>
<tr>
<td>Ag</td>
<td>961</td>
<td>1120</td>
<td>3.30 \times 10^{-6}</td>
<td>3.67 \times 10^{-9}</td>
<td>--</td>
<td>2.07 \times 10^{-4}</td>
<td>16,20-3</td>
</tr>
<tr>
<td>Ag</td>
<td>938</td>
<td>1131</td>
<td>2.11 \times 10^{-6}</td>
<td>4.90 \times 10^{-9}</td>
<td>--</td>
<td>1.22 \times 10^{-4}</td>
<td>20-3</td>
</tr>
<tr>
<td>Cu/C</td>
<td>1083</td>
<td>1430</td>
<td>nil</td>
<td>5.61 \times 10^{-9}</td>
<td>--</td>
<td>2.46 \times 10^{-4}</td>
<td>16,24-8</td>
</tr>
<tr>
<td>Ni/C</td>
<td>1318</td>
<td>1799</td>
<td>4.1 \times 10^{-7}</td>
<td>6.87 \times 10^{-10}</td>
<td>0.07</td>
<td>( \bar{B} ) taken.</td>
<td>16,18,29-31</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1736</td>
<td>1930</td>
<td>nil</td>
<td>1.24 \times 10^{-8}</td>
<td>--</td>
<td>5.9 \times 10^{-6}</td>
<td>14,21,32-34</td>
</tr>
</tbody>
</table>

*Reference 17's value of \( \gamma = 769 \text{ erg/cm}^2 \) at \( 247^\circ \text{C} \) was used with \( \gamma/\partial T = -0.3 \text{ erg/cm}^2 \text{ deg.} \)

As mentioned earlier, the chosen mathematical model, Eq. (1), corresponds to an infinite series of sawteeth of outline cc. How well this model represents the groove (Fig. 1) has been investigated in two cases calculated for the groove in a plane (\( k = \infty \)) to avoid the disturbing effect of cylindricality. It is inferred that doubling \( c \) should appreciably affect the calculated \( y \) at \( x = 0 \) to the extent that transport processes are appreciable to \( x = 0 \) from a distance \( c \), that is, where the discrepancy exists between Eq. (1) and the groove. The method of finite differences [Eqs. (23), (24), and (4)] was used for this purpose because that method is the most accurate of this paper. Increasing the value of \( c \) from 10 to 20 mils decreased the calculated value of \( y \) no more than 0.2% up to \( y = 1 \) mil in the case of zinc in which mechanism \( E_1 \) dominates. However, the same change in \( c \) decreased the calculated value by 14% at \( y = 1 \) mil in the case of Pt/C in which volume diffusion in the solid is preponderant. The higher dependence on \( \omega \propto \frac{1}{c} \) is apparently responsible. As \( y \) increases, each bottom corner of the groove acts, to some extent, as a sink for the other; rather than as a source although the model does not take cognizance of this fact. It is thought that the calculated value of \( y \) at \( y = 1 \) mil is thereby too high by less than \( \sim 1/2\% \) for Zn, \( \sim 10 \) to 20% for Cu/C, Ni/C, and Pt/C, and \( \sim 5\% \) for the intermediate case of silver. An improved model, that is, a replacement for Eq. (1), might be sought, but it would probably lead to unwarranted complication because comparable errors may result from the assumption of isotropy for surface tension and diffusion coefficients. As noted following Eq. (6) and as described in Sec. IV, the present melt wires do not perfectly fulfill the conditions for case \( E_1 \). The total error in \( y \) at \( y = 1 \) mil is probably \( \sim 20\% \) for all of the present melt wires. Fortunately, such errors are not critical for our purpose.

It is believed that the radiation enhancement of scratch smoothing of melt wires has been small in UHTREX. The maximum flux of fast neutrons has been about \( 3 \times 10^{13} \) neutrons/cm² sec. That the effect is negligible can be shown to hold for the surface diffusion of Cu/C and Ni/C, for example, during the usual maximum time in UHTREX of a few days.

IV. Experimental

There was often some recrystallization in the melt wires of UHTREX and in the experimental work to be described below. However, these effects did not seriously interfere with the observations of melting in the UHTREX experiments or observations of scratch smoothing in the present studies.

Melt wires of silver were chosen to test the calculations because of the easily maintained temperature, the convenient length of time, and (compared with zinc) chemical inertness. Calculations had indicated the growth...
of y to be about one-third due to vapor transport (E<sub>1</sub>) and two-thirds due to volume diffusion in the solid for the times of measurement. Machined wires of 99.99+% purity were freed of dissolved oxygen in a 1-h treatment at 800°C in 1 atm of hydrogen. The small steam bubbles (39) produced (Fig. 4) were not considered numerous enough to measurably retard volume diffusion in the solid, particularly at the bottom corners of the grooves. Five wires were microphotographed and microradiographed and then sealed in quartz capsules under 1 µ or less of pressure. The encapsulated, metal-bright wires were equilibrated at 938 ± 3°C. It is believed that chemisorbed impurities on the surface at this temperature would be small and would only slightly affect the transport through mechanisms E<sub>1</sub> and surface diffusion. Traces of surface oxygen would go to the gas phase or bulk silver to leave negligible concentrations either at the surface or in the bulk. The hydrogen treatment should have left the surfaces free of chloride and sulfide. Residual hydrogen was probably beneficial in removing the remaining oxygen and surface sulfide, the latter of which could have enhanced the small effect of surface diffusion. A small pressure of hydrogen would have affected mechanism E<sub>1</sub> only slightly, particularly in view of the large ratio of molecular weights of silver vapor compared with hydrogen. By comparison, having a dynamic vacuum probably would have vitiated mechanism E<sub>1</sub>. Initially, the value of y was experimentally 0.0 to 0.2 mil principally due to limitations in machining the groove to the desired shape. This effect corresponded to an error in time of 0 to 1 day. The observations (Fig. 3) were made by microradiography at the indicated intervals. The inside of the quartz capsule often developed deposits of silver due to mass transport through the vapor. The deposits above the groove may have caused about one-half the growth of y that was due to mechanism E<sub>1</sub>. Because the inside diameter of the capsules was about 42 mils, this "source" for mechanism E<sub>1</sub> had a curvature not of zero as assumed in the theoretical development, but a small negative value of about 10% of the initial value for each Fourier component. It may be difficult to estimate this error in detail, but it is likely that y was overestimated because of it. In two cases, the melt wires actually melted but this coincided with the silicon content of the wires rising from about 8 to 800 ppm. It is thought that the latter increase derived from a reaction with the quartz capsule such as

\[
\text{SiO}_2 + 2\text{H}_2\text{(trace)} = \text{Si}^{\text{(in Ag)}} + 2\text{H}_2\text{O(g).}
\]

It is inferred that 800 ppm of silicon in silver exceeds the solid solubility and gives rise to liquid and melting in the Ag-Si system the eutectic of which is at 830°C. Such wires were excluded from further consideration. Among other reasons for the fairly large standard deviations in the plotted values of y are (1) the variation of volume diffusion and surface tension with the orientation of the grains at the corners, (2) the inherent difficulty of the measurements, and (3) the necessity to discard a broken melt wire. Nevertheless, the measurements support the calculations within the limits of accuracy.

V. Discussion

Some of the foregoing equations are applicable to other geometries when the geometry is represented in terms of Fourier components y<sub>n</sub> and ∂y<sub>n</sub>/∂x = 0 at the point of interest. General applicability holds for Eqs. (16), (20), and (22) provided that the scratch is in a plane.

Further remarks regarding the present melt wires and unalloyed metals in general should be made. If the vapor pressure of the melt wire is less than 10<sup>-6</sup> atm, then the scratch smoothing near the melting point is dominated by volume diffusion in the solid in the present geometry. This is illustrated with Ag, Cu/C, Ni/C, and Pt/C for which surface diffusion is of secondary importance. It also appears that the parameter C = γΩΔν/kT of Eqs. (17) through (20) is of the same order of magnitude (∼10<sup>-15</sup> cm<sup>3</sup>/sec) for each of the present metals at its normal melting point. This is true within a factor of 2. For example, values of C from Table I and associated data are 1.5 x 10<sup>-15</sup> cm<sup>3</sup>/sec for zinc, 7.97 x 10<sup>-16</sup> cm<sup>3</sup>/sec for silver at 961°C, 5.40 x 10<sup>-16</sup> cm<sup>3</sup>/sec for Cu/C, 1.38 x 10<sup>-15</sup> cm<sup>3</sup>/sec for Pt/C at 1736°C (1.77 x 10<sup>-15</sup> cm<sup>3</sup>/sec for platinum at 1769°C). An apparent exception for Ni/C is due to this eutectic's being 135°C below the melting point of pure nickel at which temperature it has 3.2 x 10<sup>-16</sup> cm<sup>3</sup>/sec for C. That the above approximate value for C should hold for most metals having a vacancy mechanism for D<sub>v</sub> is better understood when one examines the quantities that define C. First, Shewmon...
has expressed a crude rule that the volume-diffusion coefficient $D_v$ is usually about $10^{48}$ cm$^2$/sec at the melting point of a metal. For example, this rule is obeyed within a factor of 2 for the metals of Table I except for the inapplicable case of Ni/C. Second, the surface tension at the normal melting point can be shown to be proportional to the normal melting temperature. In analogy with Mullins' approach, the (100) face of a crystal can be shown by a method of Cottrell to have

$$\gamma_s = \Delta H_{\text{sub}}/3N_a - T_s,$$  \hspace{1cm} (27)

where $\Delta H_{\text{sub}}$ is the molar heat of sublimation and $S = -d\gamma_s/dT$ is the surface entropy per unit area. Cottrell gives a typical value for $S_s$ of about 0.3 erg/cm$^2$-deg. It will be assumed that Eq. (27) represents the average surface tension of the solid although values of $\gamma_s$ calculated with individual values of $\Delta H_{\text{sub}}$ are only about 60% of the measured values for fcc metals silver, copper, nickel, platinum, and gold.$^{16,35,44,46}$ (Also see Table I.)

The discrepancy may be due principally to the employed value of $S_s$. Figure 5 shows that $\Delta H_{\text{sub}}$ at the melting point of a pure metal varies approximately as the melting temperature for fcc and other metals, giving $\Delta H_{\text{sub}} \approx 2.3 \times 10^9$ T erg/mole. One then obtains $C \approx 2.3 \times 10^{-4} a_0 (1 - 2 \times 10^{-14} a_c^2)$ cm$^3$/sec, from which $C \approx (6-4) \times 10^{-16}$ cm$^3$/sec for $a_0 = 3-6$ Å. This derivation of the value of $C$ would probably be closer to $10^{-15}$ cm$^3$/sec if it were not for the approximations for $S_s$. The rule $C \approx 10^{-15}$ cm$^3$/sec is probably also valid for other crystal structures if $D_v$ is determined by a vacancy mechanism. Otherwise, $C$ should be correspondingly less.

One can set an approximate time for objectionable scratch smoothing ($y \approx 1$ mil) in the case where the vapor pressure of the melt wire is less than $10^{-6} A_y$ and $C \approx 10^{-15} A_y$ cm$^3$/sec. Then Eqs. (23), (24), and (4) give this time as about $10^{-7}$ sec $\approx 4$ months. Although this rule is obeyed in Fig. 3 for Cu/C within a factor of 2, it is less applicable to Pt/C because of a $33^\circ$C eutectic depression, although the rule is obeyed there also. The rule is not obeyed for Ni/C principally because of the aforementioned eutectic depression of $135^\circ$C. Generalizing from $C \approx 10^{-15}$ cm$^3$/sec and $y = 1$ mil at 4 months, one should usually have no difficulty using nonvolatile, unalloyed melt wires for less than 1 month as in UHTREX. The prediction is particularly conservative if $D_v$ is not determined by a vacancy mechanism.

If the melt wire's vapor pressure is greater than $10^{-6} A_y$, this contribution may still be nil if there is a cover gas and lack of convection as in case E. For example, UHTREX's 500 psi of helium has provided a cover gas over all graphite-encased melt wires.$^{36}$ As in the above generalization for $C$, one can say that $A'$ of Eqs. (12) through (16), (23) through (26), (30), and (31) will remain less than $C \approx 10^{-15}$ cm$^3$/sec in 500 psi of helium if the vapor pressure of the melt wire is less than $10^{-3}$ $A_y \approx 1$ mm Hg. However, convection could considerably increase the vapor transport. Vapor transport is greatest when the melt wire has been vacuum-sealed in quartz, for example. Then, typically, case E1 and Eq. (6) apply. In this case, vapor transport will still be secondary at the melting point if the vapor pressure is less than about $10^{-6} A_y$.

VI. Conclusions

The scratch smoothing of grooved melt wires has been calculated to assess its interference with the detection of melting. The higher-order terms omitted in Mullins' original treatment of the general subject have been retained for the more accurate calculations. The differential equation describing the time behavior of the diagonal build-up $y$ of material at the bottom corner of the groove has been solved for zinc, silver, Cu/C, Ni/C, and Pt/C by the method of finite differences as well as by more approximate methods. The calculations have shown that the cylindricality of these melt wires stops or hinders the decay of each Fourier component $y_n$ of $n \approx 1$ at a certain fraction ($\approx 1/8$) of its original value. Positive errors result in the estimation of $y$ because of deficiencies in the representation of the groove and in meeting the conditions for estimating vapor transport in case E1. Because of these errors and those errors from the assumption of isotropy, it is believed that the total error for all of the present wires is $\approx 20\%$ at $y = 1$ mil, but less at lower values of $y$. The calculations of $y$ have been approximately confirmed with some experimental measurements on silver melt wires.

The calculated times for $y = 1$ mil are estimated for the five materials for which data are available. When vapor transport is not a factor, the smoothing can usually be well approximated at the melting point by Mullins' parameter $C = \gamma_s D_v / kT$ where $D_v$ is by a vacancy mechanism. It is shown that the surface tension of a pure, solid metal is proportional to the normal melting temperature and that $C \approx 10^{-15}$ cm$^3$/sec if $D_v$ is by vacancies. From this, the smoothing of nonvolatile, unalloyed melt wires of the present design should not be a serious problem for at least 1 month.
Acknowledgments

The author is indebted to several people of the Los Alamos Scientific Laboratory for various aspects of this work. In particular, I thank M. L. Trombetta for his solution of the differential equations by the method of finite differences, and R. Wilhelm for his computer calculations of other aspects of the problem. Certain experimental work was done by P. G. Salgado and L. R. Bergamo.

APPENDIX

THE PLANAR CASE APPROXIMATED WITH INTEGRATION

Attention is again restricted to \( x = 0 \) for which \( \Delta y = y \) and

\[
y_{pl.} = \sum_{n=2}^{\infty} y_n - \sum_{n=2}^{\infty} y_{n,0},
\]

(28)

where \( y_{n,0} = -2^{3/2}c/\pi^2n^2 \). Replacing the summations with integrals would be too inaccurate if \( y_n \) and \( y_{n,0} \) for \( n = 1 \) were included. Instead, only terms beyond \( n = 1 \) will be integrated as follows.

\[
y_{pl.} \approx y_1 - y_{1,0} + \frac{1}{2} \int_{n=2}^{\infty} y_n \, dn - \frac{1}{2} \int_{n=2}^{\infty} y_{n,0} \, dn .
\]

(29)

The interval of 2 for \( n \) in Eq. (28) is responsible for Eq. (29) having a coefficient of 1/2 for each integral and a lower limit of integration of \( n = 2 \).

The transport process will be designated \( i = 2 \) for mechanism \( E_1 \), \( i = 3 \) for mechanism \( E_2 \) or volume diffusion in the solid, and \( i = 4 \) for surface diffusion. Then, Mullins' approximation, applicable for the groove in a plane, may be written as

\[
\partial y_n / \partial t \approx -y_n \sum_i \kappa_i \omega^i,
\]

where \( \kappa_1 = A \), \( \kappa_2 = A' + C \), and \( \kappa_3 = B \). Because \( y_{1,0} = -2^{3/2}c/\pi^2 \), the first term on the right of Eq. (29) is

\[
y_1 \approx -(2^{3/2}c/\pi^2) \exp \left\{ -[A\omega_1^2 + (A' + C)\omega_1^3 + B\omega_1^4]t \right\} ,
\]

where \( \omega_1 = 2^{3/2}\pi/c \). After integrating the rightmost term of Eq. (29), one has

\[
y \approx (2^{3/2}c/\pi^2)(1 - \exp \left\{ -[A\omega_1^2 + (A' + C)\omega_1^3 + B\omega_1^4]t \right\} )
\]

\[+ \frac{c}{2^{3/2}\pi^2} - \frac{2^{3/2}c}{\pi^2} \int_{n=2}^{\infty} n^2 \exp - (t \sum_i \kappa_i \omega^i) \, dn . \]

(30)

To readily evaluate the remaining integral in Eq. (30), it will be assumed that one smoothing effect is dominant, that is, \( \sum \kappa_i \omega^i \) will be replaced by \( \kappa_i \omega^i \). The solution involves an incomplete gamma function.

\[
y \approx \frac{c}{2^{3/2}\pi^2} \left\{ 4(1 - \exp \left\{ -[A\omega_1^2 + (A' + C)\omega_1^3 + B\omega_1^4]t \right\} )
\]

\[- R_2 \exp(-R_2) \left\{ i/[i(i-1) + i^2 R_2/(i-1)(2i-1)] \right\}^2
\]

\[+ j^2 R_2^2/(i-1)(2i-1)(3i-1) + \cdots \]

\[+ 1 - \exp(-R_2) + R_2 \frac{1}{i} \Gamma(2-1/i) \}
\]

(31)

where \( R_2 = 2^{i/2}(2^{3/2}\pi/c)\kappa_4 \). The series in Eq. (31) converges fairly rapidly for \( y/c \approx 0.1 \) for which the equation agrees to within 3% with Eq. (26) if only one means of mass transport is operative.
References


11. E. P. Lane, Metric Differential Geometry of Curves and Surfaces, (University of Chicago Press, Chicago, 1940), Chap. 3.


