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On the influence of dislocations on the thermal migration of liquid inclusions

In a recent paper on the annealing of liquid lead inclusions in an aluminium lead alloy, McLean and Loveday [1] found that the inclusions migrated in the thermal gradient, produced by the electron beam, in the hot stage of a high voltage electron microscope. Those inclusions that were larger than $0.8\,\mu m$ radius migrated at a velocity independent of the droplet size, the expected result for diffusion-controlled thermal migration [2]. However, droplets smaller than $0.8\,\mu m$ migrated more slowly, apparently indicating some measure of interface inhibition of the thermal migration [2], and droplets smaller than $0.1\,\mu m$ did not appear to move at all. This is an extremely surprising result as the weight of experimental and theoretical evidence suggests that the solid–liquid interface in metals and other low entropy of melting materials is extremely mobile (e.g. [3–6]).

There are two models of the solid–liquid interface migration, the one used by McLean and Loveday [1] following, for example, Tiller [7], for kinetically faceted interfaces which requires an emerging screw dislocation to provide a spiral ledge at which solidification (for liquid inclusions, melting [8]) can occur. This leads to a relationship between the interface velocity, v_i, and the interface undercooling (or superheating), ΔT_i, given in Equation 1, where μ_2 is the appropriate mobility.

$$v_i = \mu_2 \Delta T_i^2 \qquad (1)$$

If the interface is atomically rough as expected for metals [6], then much faster interface kinetics are expected with

$$v_i = \mu_1 \Delta T_i \qquad (2)$$

McLean and Loveday reported initially a value of μ_2 that was $0.09\,\text{mm sec}^{-1}\,\text{K}^{-2}$ but following a correction of a mistake in their paper [1a] that changed the observed value of the temperature gradient from $1.85 \times 10^4\,\text{K m}^{-1}$ to $1.85 \times 10^5\,\text{K m}^{-1}$, the value of μ_2 fell by a factor of 100. This new value of μ_2 is unacceptable both theoretically and, more significantly, experimentally, since it would indicate the need for undercoolings for aluminium solidification that are much larger than the vanishingly small values found in practice [3–6], a result recently confirmed yet again in aluminium by Burden and Hunt [9]. Burden and Hunt reported that they could find no measurable undercooling (less than 0.1 K) for an aluminium casting that froze at something like $0.5\,\text{mm sec}^{-1}$ *, which if μ_2 was either 0.09 or $9 \times 10^{-4}\,\text{mm sec}^{-1}\,\text{K}^{-2}$ would need undercoolings of 2.3 or 23 K respectively.

If McLean and Loveday's results are re-analysed

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*This velocity was estimated from the ratio of latent heat of fusion to the liquid specific heat of aluminium (365 K) and from the observation that the liquid cooling rate was $625\,\text{K min}^{-1}$ so the freezing time will be about 365/625 min (35 sec) for a casting of 17 mm radius.

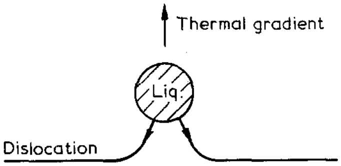

Figure 1 Inhibition of small spherical droplet by a single dislocation.

in terms of Equation 2 [7, 8], then no improvement is found as values of μ_1 of the order of 10^{-3} mm sec^{-1} K^{-1} are needed – an impossibly small value. It therefore seems that some alternative hypothesis is needed to describe the fall of inclusion velocity at small sizes and the purpose of this note is to suggest that inhibition of motion due to the *line tension* of intersecting dislocations is a more likely hypothesis. If the dislocation density has the normal value of 10^{12} m^{-2} then every liquid droplet will be less than 1 μm from a dislocation and the dislocation should have been attracted into the droplet by the strain energy released by the intersection of the dislocation with a region with zero shear modulus. Any droplet intersected by a dislocation and subjected to a local temperature gradient will start to migrate but after a migration of 1 to 2 radii, the configuration of Fig. 1 would be expected with the dislocation exerting a drag of some Gb^2 on the droplet (G, the shear modulus and $\boldsymbol{b}$ the Burgers vector).

This model readily predicts the minimum radius for migration (r_m) by equating this dislocation drag to the driving force for droplet motion. With a gradient in the liquid of G_1 and an inclusion diameter of $2r_m$ the undercooling on the back face of the just immobile inclusion is

$$\Delta T = G_1 2r_m$$

and this gives a driving force per unit area f_A (the free energy change per unit volume ΔF_v) of:

$$f_A = \Delta F_v = 2\Delta S_v G_1 r_m \ \ \mathrm{J\,m^{-3}}\ (\mathrm{N\,m^{-2}})$$

where ΔS_v is the entropy change on freezing per unit volume. By equating this force per unit area with $Gb^2/2\pi r_m^2$, the approximate force per unit area exerted by the dislocation on the inclusion, we obtain the following equation for the minimum radius:

$$r_m = \left(\frac{Gb^2}{4\pi\Delta S_v G_1}\right)^{1/3} \quad (3)$$

Using values of G of 2.7×10^{10} N m^{-2}, $\boldsymbol{b}$ of 2.86×10^{-10} m, ΔS_v of 1.15×10^6 J m^{-3} K^{-1} and a corrected temperature gradient of 1.85×10^5 K m^{-1} [1a], Equation 3 predicts a value of 0.09 μm for the minimum radius close to but somewhat smaller than the value reported – 0.12 μm [1]. The liquid phase in aluminium lead is almost pure lead, so the use in Equation 3 of the entropy of fusion of pure aluminium is somewhat doubtful. An alternative expression for r_m can be obtained from thermodynamics of solutions which gives the partial molar free energy of solid aluminium, $\bar{F}$, as

$$\bar{F} - F^\circ = RT \ln a_s$$
$$= RT \ln a_l = RT \ln c_l + RT \ln \gamma_l,$$

where F° is the free energy of aluminium in its standard state, a_s and a_l are the activities of aluminium in the solid and molten phases in Al–Pb and c_l and γ_l are the concentration and activity coefficient of aluminium in the liquid phase. If the droplet is immobile, the aluminium content of the liquid at the rear face should be raised from c_l to $[c_l + (\mathrm{d}c_l/\mathrm{d}T)\ \Delta T]$ so the partial molar free energy rises to $\bar{F}'$

$$\bar{F}' - F^\circ = RT \ln c_l' + RT \ln \gamma_l'.$$

Assuming that the supercooling makes only a negligible change in the activity coefficient, the difference in free energy per mole is

$$\bar{F}' - \bar{F} = RT \ln(c_l'/c_l) \approx RT(\mathrm{d}c_l/\mathrm{d}T)\Delta T/c_l.$$

If the molar volume is v_m then the free energy change per unit volume is given for a gradient of G_l in a droplet of diameter $2r_m$ by

$$\Delta F_v = RT \frac{\mathrm{d}c_l}{\mathrm{d}T}\frac{G_l 2r_m}{v_m c_l}.$$

The minimum radius is then

$$r_m = \left[\frac{Gb^2 c_1 v_m}{4\pi RT(\mathrm{d}c_1/\mathrm{d}T)G_1}\right]^{1/3}. \quad (4)$$

Use of the value of 10^{-5} m^3 mol^{-1} for v_m, 7.5×10^{-4} at.% K^{-1} for $\mathrm{d}c_1/\mathrm{d}t$ [1a] and 0.8 at.% for c_l [10] gives an alternative value for r_m of

0.05 μm, again somewhat smaller than the experimental value but clearly indicating that the immobility of small droplets is likely to be mainly due to the line tension of the dislocations dragged by the droplets. At larger droplet sizes the ratio of Gb^2 to the thermal gradient driving forces will be negligible (less than 10^{-3} at 0.8 μm radius) and so the diffusion controlled velocities of the large droplets are as expected. However, inhibition by *single* dislocations cannot explain the slow increase in velocity observed as the droplet size increased from 0.1 to 0.8 μm. The ratio of the retarding force due to a *single* dislocation to the force due to the thermal gradient should fall as the *cube* of the droplet radius (Equations 3 and 4). Without knowledge of the dislocation density, the average distance travelled by the droplet and the recovery kinetics of dislocations collected by the moving droplets it is difficult to make any realistic estimates of the numbers of dislocations that might be retarding droplets of different sizes but given the existing evidence for the high mobility of the solid–liquid interface in metallic systems it seems much more likely that this type of drag effect is the correct explanation of McLean and Loveday's observations* than interfacial immobility.

It would be of interest if the dislocation configuration adjacent to migrating droplets could be determined to check the mechanism postulated here.

In a series of papers on the behaviour of brine droplets in KCl crystals [11–14] Anthony and Cline reported various effects of interface kinetics but in this case for the interface between KCl and brine at room temperature there appears to be no independent evidence that suggests that some immobility might not be found. The brine droplets show clear faceting with only {1 0 0} planes exposed and following thermal migration at room temperature with an externally imposed temperature gradient of 2×10^3 K m^{-1}, small droplets (10 to 15 μm in length) did not move, while larger droplets moved at a velocity that increased, albeit irregularly, with droplet size. The smallest droplets stayed cubic with side length, l, and for such droplets a minimum side length, l_m, is readily predicted for immobility due *solely* to single dislocation drag effects from a slightly modified Equation 4:

$$l_m = \left[\frac{Gb^2 c_1 v_m}{RT(\mathrm{d}c_1/\mathrm{d}T)G_1}\right]^{1/3} \tag{4a}$$

This relationship with $G = 2 \times 10^{10}$ N m^{-2}, $b = 4.4 \times 10^{-10}$ m ($a < 1\,1\,0 > /2$) and other values quoted by Anthony and Cline [11] gives a value of l_m of only 1 μm – much smaller than the experimentally reported values of 10 to 15 μm [11]. If the retardation were due to many excess dislocations on the solidifying facet of the droplet, then over 10^3 dislocations would be needed in an area of some 100 μm^2 giving a density of excess dislocations of over 10^{13} m^{-2}. This value seems unreasonably high, but more critically if the dislocation drag were the *sole* cause of the low mobility, then by virtue of the *supersaturation* at the solidifying facet the moving droplets should show an elongation in the direction of movement, rather than a flattening due to greater undersaturation at the dissolving facet. For this reason it is to be expected that if there is any significant dislocation drag, this must be *less* than the immobility of the dissolving facet – the solidifying face is expected to show little immobility since the edges of the droplet provide a source of solidifying ledges [8, 12].

There is an interesting apparent anomaly in the work on brine droplets in KCl that gives some support to the suggestion that excess dislocations may be present on the rear face of the migrating droplets. The anomally comes from the much *smaller* values of interfacial kinetic inhibition found during shape relaxation experiments [13] following the removal of the temperature gradients. The droplets previously flattened by the migration return towards the equilibrium cubic shape but those droplets that are somewhat larger remain non-cubic. Cline and Anthony show that in this case the energy required for the interface reactions (K_s at the solidifying interface and K_D at the

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*If the dislocation density were as high as 10^{13} m^{-2}, then an inclusion of radius 0.50 μm would have collected 100 dislocations after migrating 10 μm which would only require 200 sec at a velocity of 0.05 μm sec^{-1}, provided all the intersected dislocations remained attached to the droplet.

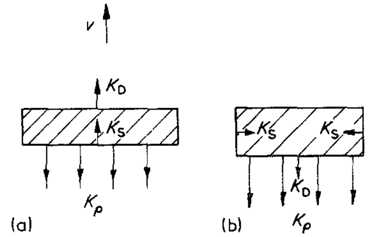

Figure 2 (a) The interfacial migration energies for movement of a liquid droplet in a temperature gradient with the excess dislocation drag K_ρ opposing the migration, and (b) for subsequent shape relaxation where the excess dislocation drag will promote the reaction.

dissolving interface) at a velocity v_i are given by

$$K = K_s + K_D = K_0 + \alpha v_i. \quad (5)$$

They obtained K_0 (for zero velocity) of 0.02 J mol^{-1} for shape relaxation experiments but values of 0.3 J mol^{-1} for K_0 for migration of a droplet in a variable temperature gradient [14] and K_0 of 0.2 J mol^{-1} for migration in an accelerational field after correction of an error in the calculation [12, 14]. That droplets of the size range 10 to 15 μm do not migrate in a temperature gradient of 2.2 K m^{-1} [11] indicates a value of K_0 (by use of Equation 10 of [11]) of 0.8 to 1.1 J mol^{-1} for the case discussed. The energy for migration in a crystal with a dislocation density, ρ, is given by

$$K_\rho = \rho G b^2 v_m. \quad (6)$$

The higher values of K_0 for migration than for shape relaxation would be expected on the model suggested here, that migrating droplets collect excess dislocations on their rear face, since such a dislocation drag (K_ρ) will oppose migration but facilitate the shape relaxation (Fig. 2).

For zero migration in a gradient,

$$K_{s,0} + K_{D,0} + K_\rho = K_0 \text{ (migration)}. \quad (7)$$

For the final shape in shape relaxation,

$$K_{s,0} + K_{D,0} - K_\rho = K_0 \text{ (relax)}. \quad (8)$$

Use of K_0 (migration) of 0.8 J mol^{-1} [11] with K_0 (relax) of 0.02 J mol^{-1} gives from Equations 7 and 8, $K_p = 0.39$ J mol^{-1} and from Equation 6 $\rho = 3 \times 10^{12}$ m^{-2} and for the smaller value of K_0 (migration) 0.3 J mol^{-1} [14], $K_p = 0.13$ J mol^{-1}, $\rho = 10^{12}$ m^{-2}. These values, though high, are reasonable and indicate that the model suggested of dislocation drag may be plausible. An obvious test of the model would be if the droplets could be given an exposure to a temperature gradient to establish a steady state shape [11] and then have their temperature gradient reversed to make the droplets migrate in the opposite direction. If there was a significant effect of dislocation drag the velocities would be initially *higher* on reversing the migration direction.

Finally, it might be noted that, independent of any role of dislocation drag effects, the empirical kinetics for interface motion observed by Anthony and Cline (Equation 6) do not appear to be compatible with any of the current models of interface migration, including that of screw dislocation movement which was found by Jones and Chadwick [8] to apply for droplet migration in the faceting material salol.

In summary, in the low driving force situation of droplet migration in thermal gradients, the role of dislocation drag on moving droplets appears to be capable of accounting for the lack of mobility of small lead droplets in aluminium but not of accounting totally for the immobility of larger brine droplets in potassium chloride, although in the latter case there appears to be evidence for dislocation drag giving different results in experiments on migration and shape relaxation.

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Crystallite orientation in heat shrinkable polytetrafluoroethylene tubing

Polytetrafluoretylene (PTFE) tubing has found extensive use as a heat shrinkable protective coating. The molecular structure of PTFE has been established by Bunn and Howells [1], and deformation mechanisms in biaxially oriented PTFE have been studied by Young [2]. We report an X-ray analysis of PTFE tubing* and discuss the behaviour of this biaxially oriented material upon thermal contraction.

Fig. 1 shows wide-angle X-ray diffraction (WAXD) photographs of PTFE tubing taken before and after heat shrinking at 365° C for 10 sec. The sharper diffraction ring corresponds to a Bragg *d* spacing of 4.9 Å; the *d* spacing does not change significantly on heating. Evidence of preferred orientation is seen in the ring; further, upon heat shrinking the position of the maximum intensity shifts 90° in the azimuthal direction. Samples having orientation maxima between these two azimuthal positions were sought with no success. During heating, the tubing underwent a large differential shrinkage amounting to 35% radially but only 5% longitudinally.

To better determine the degree of crystallite order in the axial and transverse directions of the tubing, diffraction intensity was measured along chi on an automated four-circle Picker Corporation diffractometer (Fig. 2). The orientation function $f(\chi)$ was calculated from the intensity distribution with the peak maxima assigned to 90° χ [3]. The value of $f(\chi)$ decreased on heating from 0.85 to 0.68, indicating not only a 90° change in preferred orientation direction upon heating, but also that the material loses about one-third of its molecular order. This calculation is

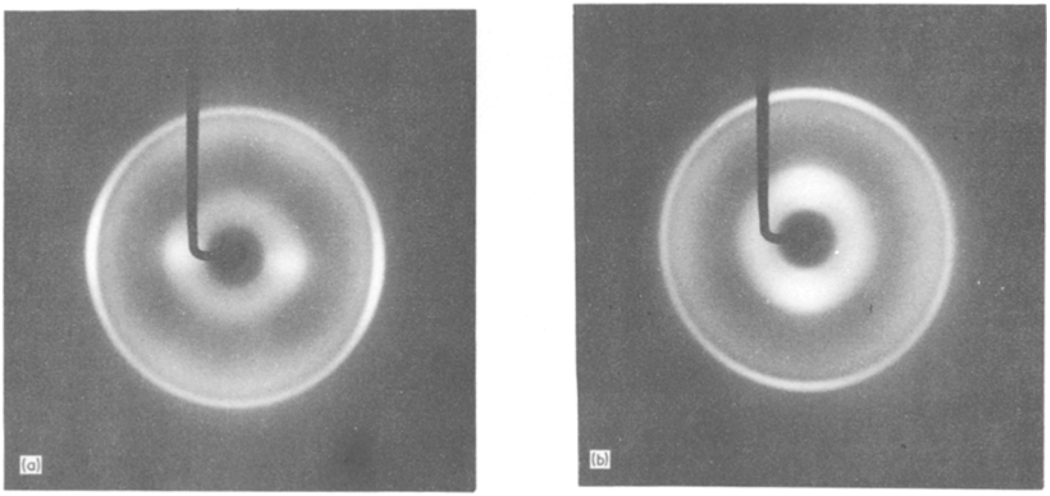

Figure 1 Wide-angle X-ray diffraction photographs of PTFE tubing: (a) before, (b) after heat shrinking at 365° C. Tube axis direction horizontal. Co*K*α radiation, exposure time 1 h.

* Kindly supplied by Alpha Wire Company, Elizabeth, New Jersey.