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Capillary shape equilibration of liquid inclusions embedded in a partly soluble solid

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We estimate the time for capillary equilibration of a liquid inclusion embedded in a solid that is partly soluble in the liquid and discuss, on this basis, data in the literature concerning liquid inclusion capillarity.

Keywords: Capillary phenomena; Diffusion (liquid); Aluminium alloys; Copper alloys; Liquid inclusion

Liquid inclusions can exert a strong influence on the mechanical properties of solid metals or ceramics. For this reason, and also because they pose interesting questions in the capillarity of materials, such inclusions have been the subject of many investigations; recent or frequently cited examples are given by Refs. [1–8].

Methods used for their microstructural characterization fall essentially into two classes: (i) hot-stage "in situ" microscopy, where microstructural information is gleaned while the inclusions are liquid, and (ii) cold-stage "*post-mortem*" studies, where solidified inclusions are characterized under the assumption that their shape has remained unchanged compared to what it was when the inclusion was molten. In both instances an important consideration is whether the liquid inclusion has had time to reach capillary equilibrium prior to observation. In the latter class of studies an additional requirement is that the inclusion shape not depart from this equilibrium shape while the sample is cooled and solidified. If these conditions are not fulfilled, the inclusion shape is off-equilibrium, which generally obscures data interpretation.

This short contribution is motivated by the fact that this issue, of liquid inclusion shape equilibration, is often glossed over. At times, the inclusion diameter is simply compared with "$\sqrt{(Dt)}$", the square root of a characteristic experiment time t multiplied with a relevant coefficient for diffusion in the liquid, D [4,5,9]. This is an oversimplification; other parameters, particularly the (typically very low) solubility of the solid in the liquid, also govern the kinetics of shape equilibration for such liquid inclusions.

Consider a binary alloy of two elements having limited mutual solubility, held at a temperature such that one is liquid while the other is solid. Assume that there are no intermetallic compounds formed between the two. If the alloy contains only a few volume per cent of liquid, the microstructure will consist of isolated droplets of one metal surrounded by a matrix of the other. For simplicity in the notation (but with no loss in generality) we call hereafter the solid metal Cu and the liquid Pb. We take the solubility of Pb in Cu to be essentially nil; however, this assumption does not affect the derivation significantly (it changes slightly the mass balance at the interface).

We want to estimate the time that it will take for a small inclusion of the liquid embedded in the solid to reach the shape dictated by capillary equilibrium. We assume that (i) the rates of diffusion through the solid and along the solid/liquid interface are negligible compared with the rate of diffusion through the liquid and that (ii) there are no kinetic limitations to movement of the liquid/solid interface. In practice, the first assumption is very realistic. The second is not always obeyed [8]; then, the derived equilibration time is a lower limit.

We also neglect the influence of elastic strain energy: the validity of this assumption depends on the system under consideration and on the temperature. With

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nanometric inclusions, misfit can significantly influence their shape, as shown in the Al/Pb system where "magic size" effects have been observed below an inclusion diameter around 35 nm [10]. With larger inclusions, in the purely elastic regime the relative importance of strain energy increases in theory compared with capillary energy; however, so does the ease of misfit dislocation nucleation in the matrix, which will lower the strain energy significantly [11,12].

The time for shape equilibration is dictated by the rate of copper diffusion through the lead. The problem was treated by Nichols and Mullins in a linear perturbation analysis of the shape of a solid sphere under the assumption of a constant interfacial energy (Table 1 of Ref. [13] with $l = 2$). We provide in the Appendix a somewhat cruder but more direct and general derivation leading to the same result. The equilibrium shape is approximately reached after time:

$$\Delta t = \frac{RT \cdot r^3}{8 \cdot D \cdot C^0_{\mathrm{Cu}} \cdot \gamma_{\mathrm{SL}} \cdot \overline{V_{\mathrm{Cu}}} \cdot \Omega_{\mathrm{Cu}}} \tag{1}$$

where RT has the usual meaning, r is the inclusion's radius, D is the volume diffusion coefficient of Cu through liquid Pb, C^0_{Cu} is the equilibrium atomic solute concentration of Cu in Pb, γ_{SL} is the solid–liquid interface energy, $\overline{V_{\mathrm{Cu}}}$ is the partial molar volume of Cu in Pb, and Ω_{Cu} is the atomic volume of copper. We note in passing that the transcription of that equation in Eq. (10) of Ref. [3] contains an obvious typographical error.

We now apply Eq. (1) to the Cu–Pb and Al–Pb systems, Figures 1 and 2. Parameters used in the calculation of these curves are as follows:

(i) *Cu–Pb system*, Figure 1 – The diffusion coefficient, D, is [14]:

$$D = 420 \cdot 10^{-9} \exp\left(\frac{-4850}{T}\right) \quad \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right] \tag{2}$$

The solid/liquid interfacial energy is computed according to the regular solution model, where [15]

$$\gamma_{\mathrm{SL}} = A + B\left(C^{\mathrm{liquid}}_{\mathrm{Cu}} - C^{\mathrm{solid}}_{\mathrm{Pb}}\right)^2 \approx A + B\left(C^{\mathrm{liquid}}_{\mathrm{Cu}}\right)^2 \tag{3}$$

in which $C^{\mathrm{liquid}}_{\mathrm{Cu}}$ and $C^{\mathrm{solid}}_{\mathrm{Pb}}$ are, respectively, the solidus and liquidus atomic concentrations in the Cu–Pb system. From the phase diagram [16] and literature data [17], we have $A = 190\ \mathrm{mJ/m^2}$ and $B = 248\ \mathrm{mJ/m^2}$. For the molar volume of copper, we simply use its value at room temperature, namely $\overline{V_{\mathrm{Cu}}} = 7.12 \cdot 10^{-6}\ \mathrm{m^3\ mole^{-1}}$.

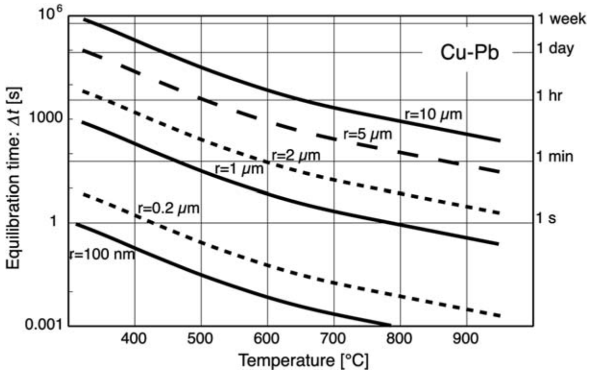

Figure 1. Estimated time for capillary shape equilibration of lead inclusions in copper, as a function of the average radius of the inclusion and temperature.

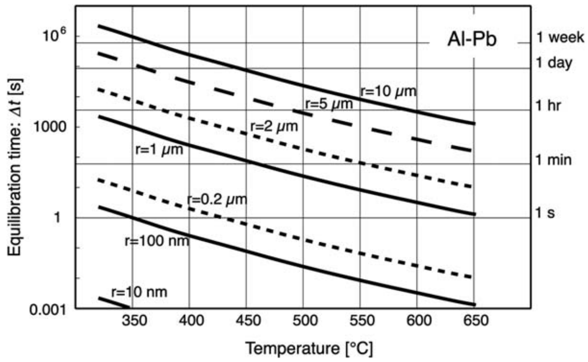

Figure 2. Estimated time for capillary shape equilibration of lead inclusions in aluminium, as a function of the average radius of the inclusion and temperature.

(ii) *Al–Pb system*, Figure 2 – The diffusion coefficient, D, is [2]:

$$D = 167 \cdot 10^{-6} \exp\left(\frac{-8780}{T}\right) \quad \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right] \tag{4}$$

The solid/liquid interfacial energy and molar volume of Al are taken as constant for the temperature range considered [2], at $0.347\ \mathrm{J \times m^{-2}}$ and $9.90 \times 10^{-6}\ \mathrm{m^3\ mole^{-1}}$, respectively.

The curves in Figures 1 and 2 give a rapid answer to the question of whether lead inclusions in these two metals have had time to equilibrate after an isothermal hold. The dependence on size is given explicitly for convenience (the curves collapse if the ratio of time to inclusion volume is used in the ordinate axis). On this basis, published data can be reexamined.

- *Spheroidization of long inclusions* – The time of spheroidization, τ, of elongated Pb inclusions in swaged Al–5 wt.%Pb was measured using X-ray microphotography on micrometric inclusions (Ø 25–75 μm) after interrupted anneals, and using in situ hot-stage TEM on smaller inclusions, 0.1–1 μm in size [2,3]. This time was found to follow a cubic ($\tau \alpha r^3$) law, indicating a process controlled by volume diffusion, and to depend on the equilibrium solubility, the diffusion coefficient, the solid/liquid interfacial energy, and the temperature in full accordance with Eq. (1).
- *Nanometric particles in transmission electron microscopy* – Nanometric particles of lead in Al or Cu have been observed by several authors in transmission electron microscopy (TEM) [5,8]. Slightly above the inclusion melting point, the corresponding equilibration times are relatively short: around one millisecond for particles 10 nm in radius, around one second for particles 100 nm in radius. At higher temperatures they are of course shorter still. Shape equilibration of nanometric particles in a hot-stage electron microscope is thus essentially instantaneous. This reinforces the interpretation offered by Gabrisch et al. for the particle shape hysteresis that was observed with very small lead inclusions in Al upon thermal