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METHODS TO DETERMINE SOLID - LIQUID SURFACE ENERGIES II

-The grain boundary groove method-

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SUMMARY

Theoretical and experimental grain boundary groove methods are discussed. The application of the methods for transparent organic materials and binary eutectic alloys are examined critically.

ÖZET

Teorik ve deneysel "grain boundary groove" metodları tartışıldı. Metodların, saydam organik maddelere ve ikili ötektik alaşımlara uygulanması incelendi.

1. INTRODUCTION

The most effective methods for measuring solid-liquid surface energy, σ_{sL}, experimentally involve the direct application of Gibbs - Thomson equation. This equation is formed by combining the condition of mechanical equilibrium of a curved interface and the condition of chemical equilibrium. If all other intensive variables (such as composition, pressure and strain energy) remain constant, a solid bounded by an interfacial element having principle radii of curvature r_1 and r_2 measured in the solid will be in equilibrium with its melt at a temperature T_r (which is not equal to the phase diagram liquids T_m) the Gibbs - Thomson equation for this is given by,

$$T_m - T_r = \Delta T_r = \frac{\sigma_{sL} V_{si}}{\Delta S} \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (1)$$

where V_{si} is the partial volume of the solid i^{th} component, ΔS is the entropy of fusion, (in the case of an alloy system weighted entropy fusion, ΔS^{*} is used instead of ΔS).

The solid-liquid surface energy, σ_{SL} can be evaluated directly from the Gibbs-Thomson equation provided that ΔT_r is measured for known values of r_1 and r_2 for a system at equilibrium and ΔS is known independantly.

A number of theoretical and experimental techniques to measure σ_{SL} have been discussed in the previous paper[1]; in fact most of the experimental techniques have based directly or indirectly on the Gibbs-Thomson equation. Probably the most attractive method of measuring σ_{SL} directly for macroscopic systems involves observing the "equilibrium shapes of grain boundary grooves" (Fig.1). These grooves are formed by the intersection of planer grain boundaries with an otherwise planar solid-liquid interface stabilised by an applied temperature gradient. At large distance away from the grain boundary groove ($5h < x < -5h$ see fig.1) the groove curvature becomes zero (i.e. : $dx/dy = 0$) so thus the interface becomes planar. The curvature of the interface towards the root groove in the x-y plane increases (curvature, r, becomes smaller) so as to balance the decreasing interfacial temperature (increasing ΔT_r) according to the Gibbs-Thomson equation. At each point on the interface in the vicinity of the groove, the local curvature is given by $(2/r) = 1/r_1 + 1/r_2$ where r_1 and r_2 are the principle radii of curvature

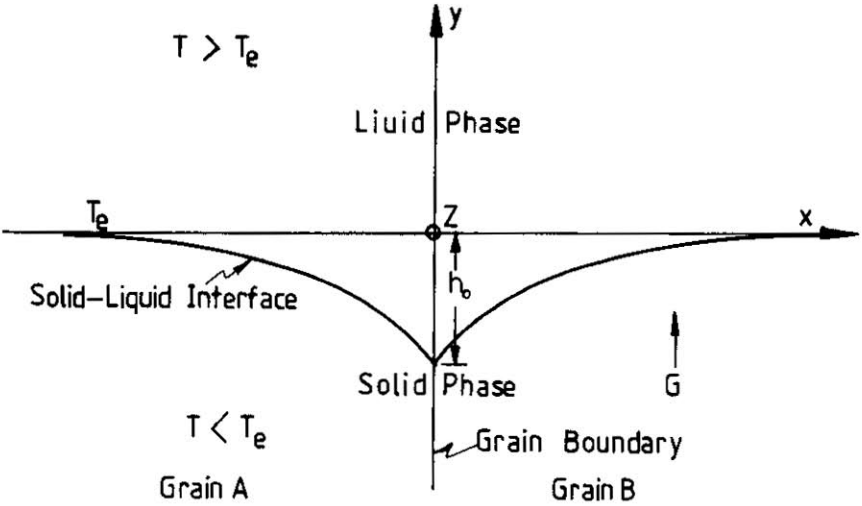


Fig.1. Schematic illustration of a grain boundary groove

For the case of a planar grain boundary intersecting a planar solid-liquid interface, $r_2 = \infty$. The remaining curvature $1/r_1$ is related to the curvature under-cooling ΔT_r from the zero curvature equilibrium temperature by the Gibbs-Thomson equation which may be written as :

$$T_{(\infty \quad 0)} - T_{(x,y)} = \Delta T_r = \frac{\sigma_{sL}}{\Delta S_f \, r} \qquad (2.)$$

where ΔS_f is the entropy of fusion per unit volume and the rest of the variables are as described before, (see also fig.1).

The equilibrium grain boundary groove shape in an applied uniform temperature gradient, in a two dimensional groove has been calculated theoretically using equation (2) by Bolling and Tiller [2] for the case $K_s = K_L$, by Nash and Glicksman [3] and Gündüz and Hunt [4] for the case $K_s \neq K_L$ (where K_s and K_L are the thermal conductivities of the solid and liquid phases respectively) and observed experimentally in situ by Jones and Chadwick [5 , 6] , Jones [7 , 8] Schaefer et al [9] Nash and Glicksman [8] and Hardy [10] . The solid-liquid surface energies have been derived from the measurements of the observed grain boundary grooves in an applied temperature gradient by these authors [4 -10] .

5.2.4.1. Grain Boundary Groove Method for $K_L = K_s$

When the thermal conductivities of the solid phase (K_s) and liquid phase (K_L) are equal, the temperature distribution in the region of the grain boundary groove is a simple linear function of "y" (fig.1) which is independent of a interface shape. This gives a linear temperature gradient, G along the y-axis and $\Delta T_r = Gy$, so thus the linear temperature distribution allows equation (2) to be integrated. This special case was solved by Bolling and Tiller (for isotropic σ_{sL}) writing equation (2) as [2]

$$\Delta T_r = Gy = -\frac{\sigma_{sL}}{\Delta S_f} y'' \left[1 + y'^2 \right]^{-3/2} \qquad (3\ a)$$

or

$$y\,[1 + y'^2]^{3/2} = K^2\,y'' \quad (\text{where } K^2 = \frac{\sigma_{sL}}{G\,\Delta S_f}) \qquad (3\text{ b})$$

A simple integration of equation (3 b) gives

$$\frac{y^2}{2} = -K^2\,[1 + y'^2]^{-1/2} + K^2 B \qquad (4)$$

where B is an arbitrary constant of integration. Bolling and Tiller have solved this equation for $B > 1$, $B = 1$ and $B < 1$ and obtained representations of the interface shapes in each case. If σ_{sL} is isotropic then $y' = 0$, when $y = 0$ and from equation (4) $B = 1$. Thus the grove (with $y' = \infty$ at $x = 0$) is described by

$$X = f(y) = K\ln\left[\frac{2K + 4K^2 - y^2}{4}\right] - (4K^2 - y^2)^{1/2} + K\,[2 - \ln(\surd 2 + 1)] \qquad (5)$$

which gives the interface shape in fig. 2.

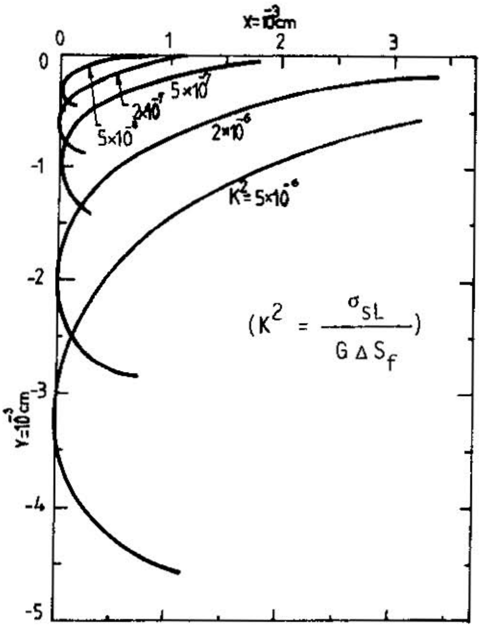


Fig.2. Interface shape for isotropic σ_{sL} and several values of K (from ref.2)

Equation (3 b) has also been integrated by Schaefer et al [9] to give the equilibrium shape of the interface surrounding the grain boundary for $K_S = K_L$. The result of this integration (for dimensionless coordinates) is

$$\mu = \frac{1}{2} \ln \left[\frac{-\eta}{1 - (-\eta^2)^{1/2}} \right] - (1 - \eta^2)^{1/2} + \frac{1}{2} \ln[\tan(\xi/2)]$$

$$+ \cos\xi \qquad (6)$$

where $\mu = X/2K$; $\eta = y/2K$; $\xi = (\pi - \varphi/4)$ the groove depth h is found to be $h = 2K \sin \xi$. For the case of $\varphi = 0$ and $= \pi/4$ the simple useful result

$$h_o = \left(\frac{2 \sigma_{sL}}{G \Delta S_f}\right)^{1/2} \qquad (7)$$

is obtained. Thus if G and h can be measured and if ΔS_f is known independently, then the solid-liquid surface energy can be calculated from equation (7). The accuracy of the method depends on the measurement of the G and h values (and thus the equilibrium condition). Consequently, a well controlled, shallow temperature gradient should be used, so that the groove depth will be large enough for accurate optical measurements 'in situ',

Schaerfer et al [9] also applied this method, to measure the solid-liquid surface energy in highly purified succinonitrile (which has equal thermal conductivities in both phases).

The value of σ_{SL} obtained was 8.94 + 0.48 erg/cm^2. This value is very different from the value of 28 + 5 erg/cm^2 obtained by Jones and Chadwick [5] with the same method for succinonitrile. This difference was explained as being due to the ΔS_f value used in the evaluation. Jones and Chadwick [5] used ΔS_f = 8.5 cal/mole K originating from the work of de Vloed [11]. Schaefer et al [9] used ΔS_f = 2.68 cal/mole K from the work of Wulff and Westrum, [12] . When the Wulff and Westrum's value was applied to Jones and Chadwick's result, a value for σ_{SL} of 9 + 2 erg/cm^2 was obtained which is in good agreement with Schaefer et al's result.

5.2.4.2. Grain Boundary Groove Method for $K_L \neq K_S$

Unfortunately values of the interfacial free energy obtained assuming equal thermal conductivities are often suspect. This is due to the fact that the Bolling and Tiller analysis is only applicable to systems where K_S and K_L are equal. When the thermal conductivities are not equal, however, there is a discontinuity in the temperature distribution and the temperature gradient at the interface.

This difficult problem was treated by Nash and Glicksman [3] in a detailed numerical analysis. The problem is formulated using dimensionless coordinates $\eta = y/\lambda$ and $\mu = x/\lambda$. The computer solutions for the interface were obtained using a solid-liquid interface intersected by a parallel array of grain boundaries spaced periodically along the X,(μ) coordinate (fig.3) with the appropriate boundary and temperature distribution conditions. The groove shape was predicted as functions of the thermal conductivity ratio R = K_S/K_L, the dihedral angle, φ and θ,(Fig. 4). θ is given as

$$\theta^2 = \sigma_{SL} \; [\lambda^2 \; \Delta S_f \; G_S]^{-1} \qquad (8)$$

where λ is the half width of a single cell and the rest of the parametres are as described before.

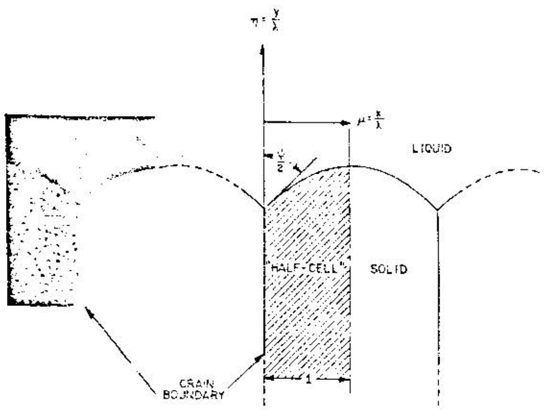


Fig.3. Schematic representation of a s-L interface by parallel array of grain boundaries (for ref.3)

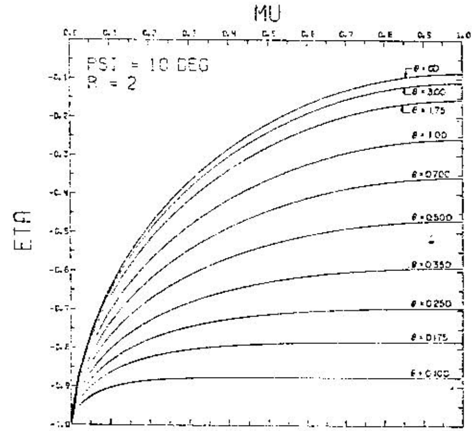


Fig.4 .Computure generated grain boundary groove profiles for various of θ (from ref.3)

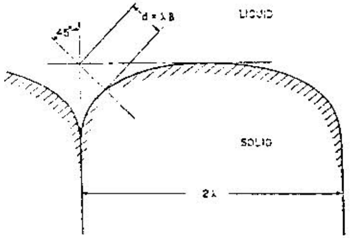


Fig.5.a.Construction employed for the determinations of the parameter from a grain boundary groove profile (from ref.3)

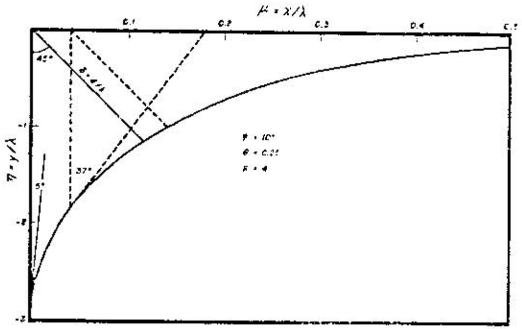


Fig.5 .b. To show how φ and d characterise the shape of a cusp (from. ref.10)

The entire calculated interface profile can be characterised by φ and a dimensionless distance δ (Fig.5) which was determined as

$$\delta = \frac{d}{\lambda} \qquad (9\ a)$$

where d is the dimensional distance from the origin to the interface along the bisector (Fig. 5).

Nash and Glicksman's method is theoretically applicable to systems having unequal thermal conductivities but it is too complicated to apply for observed groove shape for the following reasons :

a) An identical numerically calculated grain boundary groove profile must be obtained for each observed groove shape for the same R and φ values.

b) A respective θ value must be found related to δ for the same R and φ values and the dependence of δ an φ must be known.

c) For accurate σ_{sL} measurements δ must be smaller than 0.25 but larger than 0.05 (Fig. 6). In order to obtain this condition, G_S must be experimentally adjustable to obtain suitable λ and d values ($\delta = d/\lambda$).

When λ is very large compared to d, all calculations must be modified and σ_{sL} must be defined as a function of λ (Fig. 7).

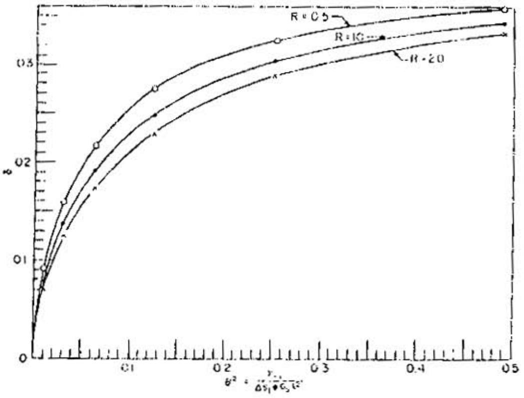


Fig. 6 verus θ for three values of R ($R=K_S/K_L$, from Ref. 3)

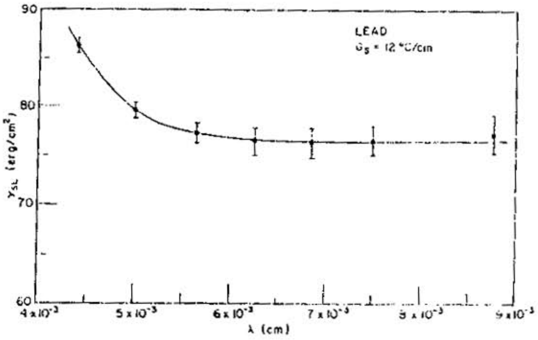


Fig. 7 .Variation of with (from ref. 3)

Yet only a few illustrative applications of the Nash and Glicksman method have been made by Nash and Glicksman for lead [3] by Hardy for ice-water [13], and Jones for various transparent organic materials [5 -8], (Fig.8).

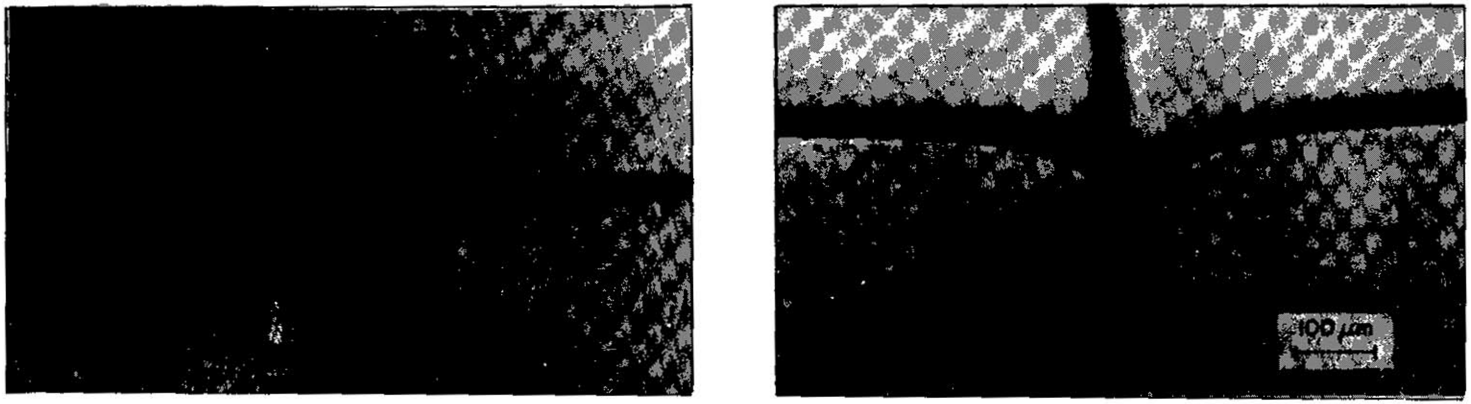
In order to obtain equilibrated grain boundary groove shapes for binary alloys, an experimental system was constructed by Gündüz and Hunt [4]. The experimental system developed involves maintaining a radial temperature gradient with minimal longitudinal temperature differences with temperature stable to within + 0.1°C up to 600°C.

The system holds the specimen in a very stable temperature field over a period of a week to achieve equilibration of microstructure and grove shape. It was necessary to ensure that the central annular liquid core was sufficiently thin to ensure an effective quench when the current supplying the axial heating element was turned off. The groove shapes where grain boundaries meet the quenched-in solid-liquid interface could then be determined by careful multiple matellographic sectioning, polishing and etching. Thermal conductivities were determined for the solid phases involved in seperate experiments using the same radial heat flow apparatus and for the liquid phases by thermal analysis during unidirectional solidification. In this way equilibrated grain boundary groove shapes, K_S, K_L and G_S values were obtained experimentally.

Gündüz and Hunt [4] numerically solved the heat flow problem through the experimentally obtained grain boundary groove shape using K_L, K_S and G_S values with appropriate boundary and temperature distribution conditions. They integrated the equation (2) in the y direction from the flat surface to a point on the cusp (Fig.9). That is ;

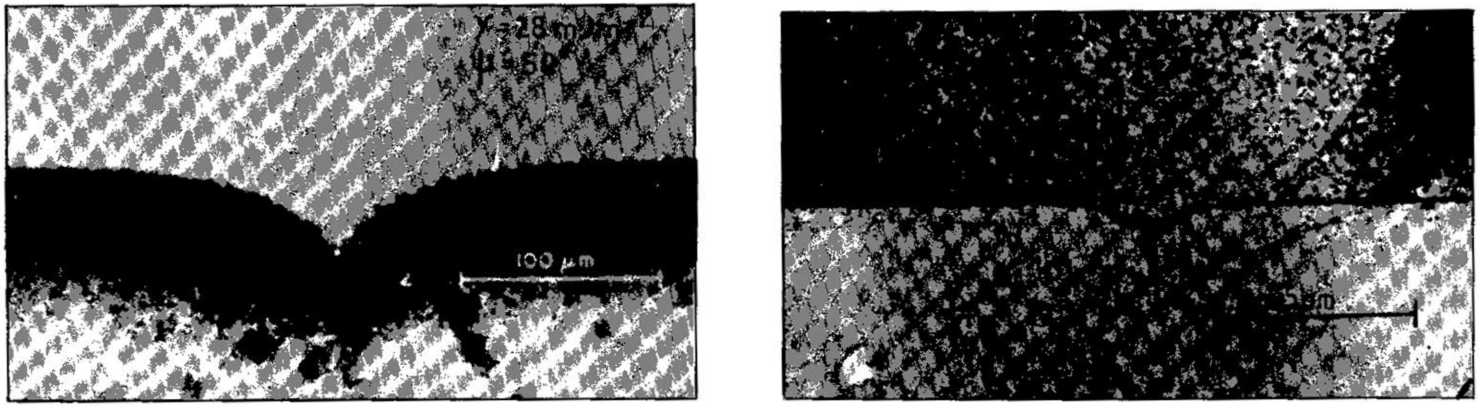
$$\int_{0}^{y} \Delta T_r \, dy = A \int_{0}^{y} \frac{1}{r} \, dy \quad (\text{where} \quad A = \frac{\sigma_{sL}}{\Delta S_f}) \qquad (11)$$

A finite difference method was used to calculate the difference in temperature between the flat surface and points on the groove shape. The numerical method presented by Gündüz and Hunt [4] merely calculates



a)Champhane (from ref.5)

b) Succinonitrile (from ref. 9)



c)Ice-water (from ref.10)

d) Lead-bi-Crystal (from ref. 3.)

Fig. 8. Observed grain boundary groove shapes

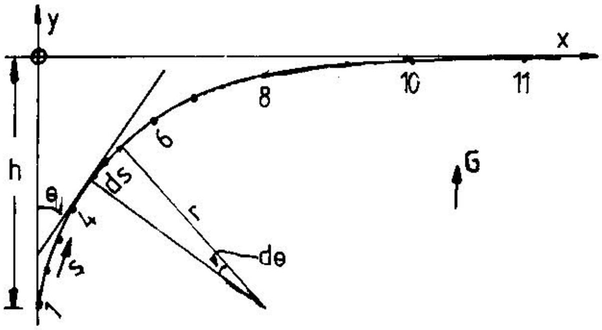


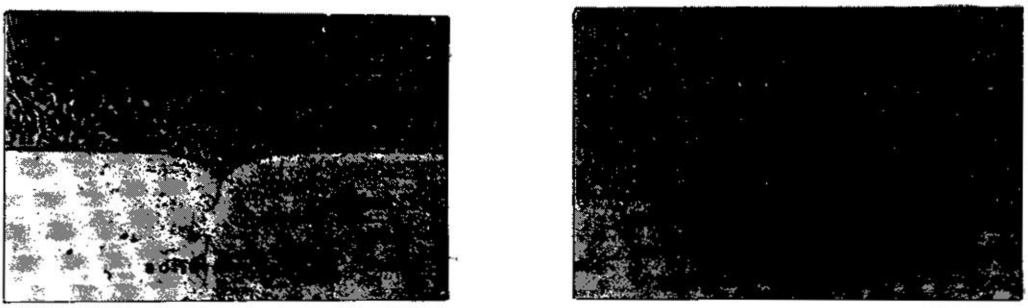
Fig.9. Showing the defination of θ dθ, ds, X,y and the points used for the calculation (from ref.4)

the temperature along the interface of a measured equilibrium shape rather than attemp to predict the equilibrated groove shape. The numerical method allows to obtain A for any equilibrated groove shape in a applied temperature gradient provided that the temperature gradient G_S the thermal conductuities of the phases K_L and K_S and the actual size of the groove is known. Then σ_{sL} is obtained from $A = \sigma_{sL}/\Delta S_f$.

Gündüz and Hunt also applied the finite difference method to measure σ_{sL} in Al-Cu, Al-Si and Pb-Sn systems, (Fig.10). This numerical method was used to analyse grain boundary grooves obtained by other workers [3, 9, 10]. Gündüz and Hunt's numerical method gave the results similar to those given by the Nash and Glicksman's method.

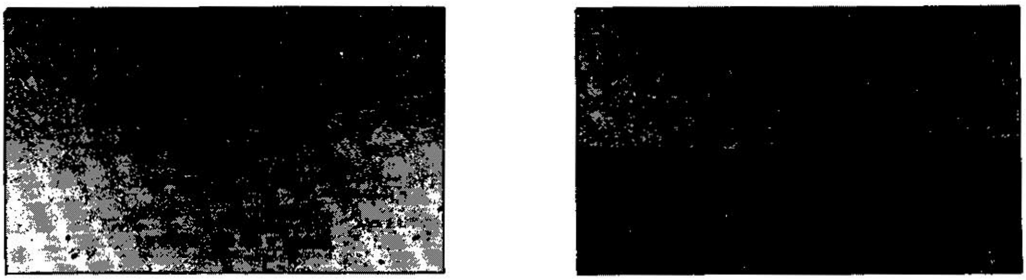
CONCLUSION

The measurement of the solid-liquid surface energy σ_{sL} is not easy and values obtained using different methods (even using the same method) of measurement shows variations as great as 50 % (see Table-1, and ref. 1). None of the methods, except the grain boundary groove method is suitable to use for measuring σ_{sL} for the macroscopic systems.



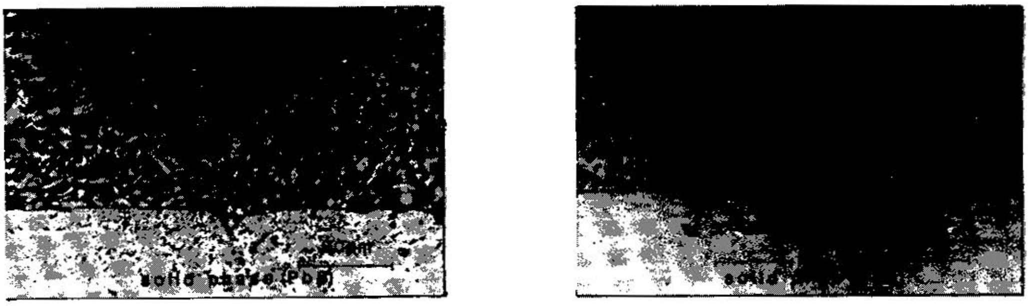
a) Solid Al-Liquid AlCu, G=20.36 ^{0}C/cm
σ'_{SL} = 160.69 erg/cm^2, σ'' = 147.80 erg/cm^2

b) Solid CuAl$_2$- liquid AlCu, G=17.69 ^{0}C/cm
σ' = 103.68 erg/cm^2, σ''_{SL}=100.80 erg/cm^2



c) Solid Al-liquid AlSi, G=7.71 ^{0}C/cm
σ'_{SL} = 157.75 erg/cm^2 σ''_{SL} = 193.95 erg/cm^2

d) Solid Si-liquid AlSi, G=37.04 ^{0}C/cm
σ'_{SL} = 416.60 erg/cm^2, σ''_{SL} = 412.53 erg/cm^2



e) Solid Pb-liquid PbSn, G=13.64 ^{0}C/cm
σ'_{SL} = 49.14 erg/cm^2, σ''_{SL} = 64.65 erg/cm^2

f) Solid Sn-liquid PbSn, G=6.41 ^{0}C/cm
σ'_{SL} = 121.18 erg/cm^2, σ''_{SL} = 116.57 erg/cm^2

Fig.10. Observed grain boundary groove shapes for binary eutectic systems (from ref.4) ($\overset{LHS}{\sigma_{SL}} = \sigma_{SL}'$ $\overset{RHS}{\sigma_{SL}} = \sigma_{SL}''$)

Table.1. Measured solid-liquid surface energies (erg/cm²)

Meterials		From Homogereous Nucleations	From Experimental Determination	From Crystal Growth
Stearic acid			105 to 150 [28] 150 ± 10 [29]	
Myristic acid			90 ± 10 [28] 70 ± 5 [29]	
Lauric acid			21.7 ± 2.0 [30]	
Benzene		20.4 [18]	22 ± 2 [30] 44 ± 10 [8]	5 [8]
Ice-water		26.1 [19] 24.2 [6] 30.8 [18]	44 ± 10 [8] 29.1 ± 0.9 [10] 41 ± 9 [5] 33 ± 3 [26] 33.7 [36]	16 to 25 [20, 21] 20 ± 2 [24]
White phosphorus		12.6 [18]	10.5 ± 2.0 [5] 12 ± 2 [8]	0.93 ± 0.05 [25] 0.7 [22]
Camphane			6 ± 1 [8] 5.3 ± 0.9 [5]	
Succinonitrile			28 ± 5 [5] 28 ± 4 [8] 8.94 ± 0.5 [9] 7.47 [36]	
Naphthalene		30.1 [18]	66 ± 11 [8]	
Diphenyl		24 [18]	50 ± 10 [8]	
Ethylene Dipromide		21.0 [18]	35 ± 7 [8]	
Carbontetrabromide		10.7 to 21.8 [18]	10 to 20 [8]	
Tin		54.5 [14] 59 [16] 65 [15] 70.6 [35]	62 ± 10 [31]	49 to 61 [23]
Lead		33 [14] 69 [17]	40 ± 7 [33] 76 [3] 56.2 [4] 78.3 [36]	34.6 to 42.7 [23]
Gold		132 [14]	270 ± 10 [34]	
Bismuth		54 [14] 60.2 [16] 79.3 [35]	55 to 80 [32] 61.3 [27]	
L.Phase	S.Phase	-	163.4±21.2 [4]	
AlCu	Al	-	163.4±21.2 [4]	
	$CuAl_2$	-	87.8±10.8 [4]	
AlSi	Al	-	168.9±20.0 [4]	
	Si	-	352.4±38.4 [4]	
PbSn	Sn	-	132.4±18.9 [4]	
	Pb	-	56.2±8.2 [4]	

The grain boundary groove method allows σ_{SL} to be measured for multi-component systems as well as for pure materials, for opaque systems as well as for transparent materials, for any observed grain boundary groove shape. The measurement of σ_{SL} using Bolling and Tiller's method (grain boundary groove technique with equal thermal conductivities, $K_S=K_L$)is only applicable for systems having aqual solid and liquid thermal conductivities. Nash and Glicksman's method is theoretically applicable to systems unequal thermal conductivities but it is too complicated to apply for any observed groove shape. Gündüz and Hunt's method allows to obtain A, numerically for any equilibrated grain boundary groove shape for any R ($R = K_L/K_S$) value by just knowing G and actual size of the groove shape. Then solid-liquid surface energy, σ_{SL} can be evaluated from $A = \sigma_{SL}/\Delta S_f$ if ΔS_f is konwn independently.

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