

GTT Workshop 14-16/Sep/2011

***Estimation of Solid-liquid Interfacial
Energies of Alloy Systems from
Thermodynamic Properties***

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(T.Tanaka, A.Fukuda, M.Suzuki: *Int. J. Mat. Res.*, to be submitted)

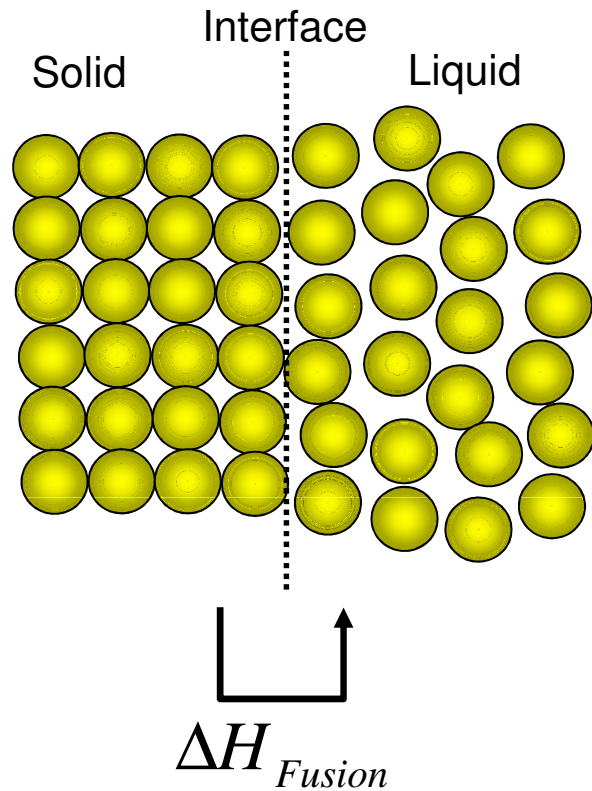
Number of published reports on interfacial properties

	Expe. data	Estimation
▪ Surface tension of pure metals:	◎	◎
▪ Surface energy of pure solid metals:	○	○
▪ Surface tension of liquid alloys:	◎	◎
▪ Surface energy of solid alloys:	△	△
▪ Surface tension of molten slag:	◎	○
▪ Interfacial energy between metal and slag:	◎	○
▪ Solid-liquid interfacial energy of pure metals:	○	△
▪ Solid-liquid interfacial energy of alloys:	×	×
	(Very limited)	

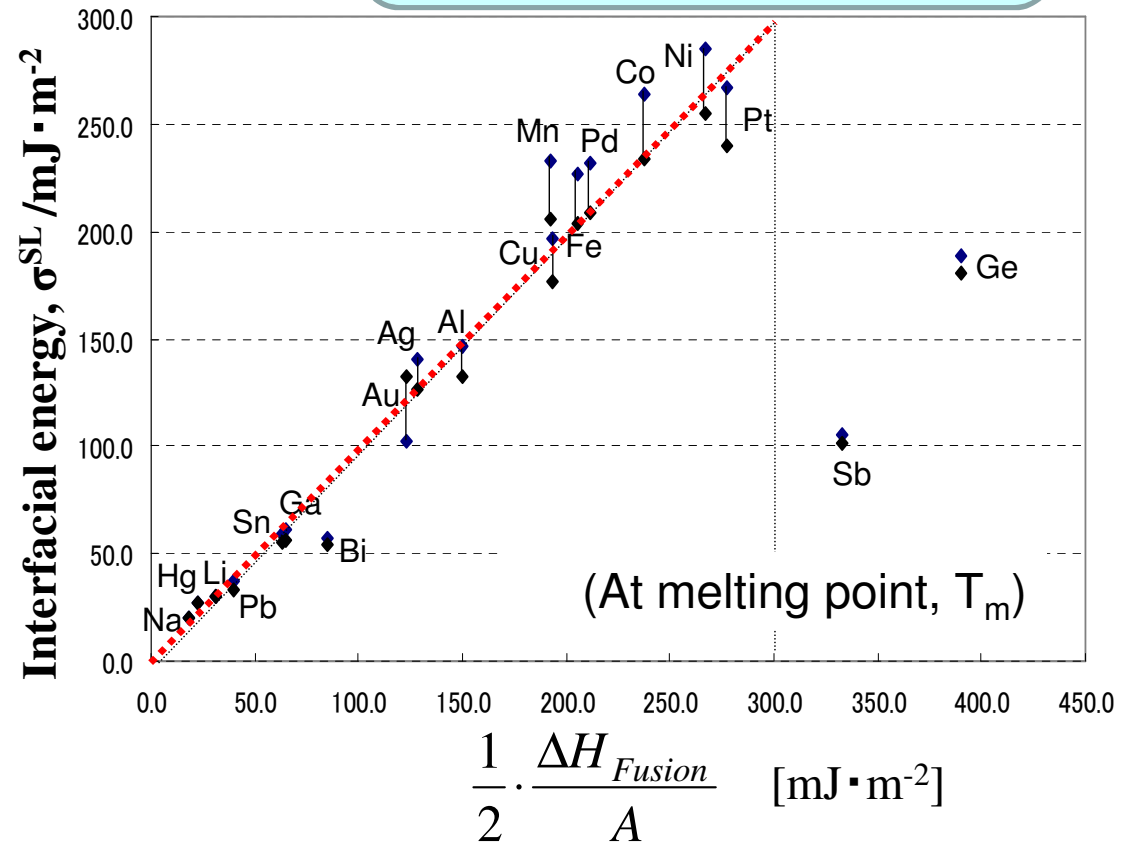
Evaluation of Solid-liquid Interfacial Energy of Pure Metals

based on Enthalpy of Fusion

(Turnbull et al., 1950)



$$\sigma^{Liq-Sol} = \frac{1}{2} \cdot \frac{\Delta H_{Fusion}}{A}$$



*D. Turnbull and R.E. Cech :
J. Appl. Phys., 21 (1950), 804.

*D. Turnbull : J. Appl. Phys.,
21 (1950), 1022.

Aim of present study:

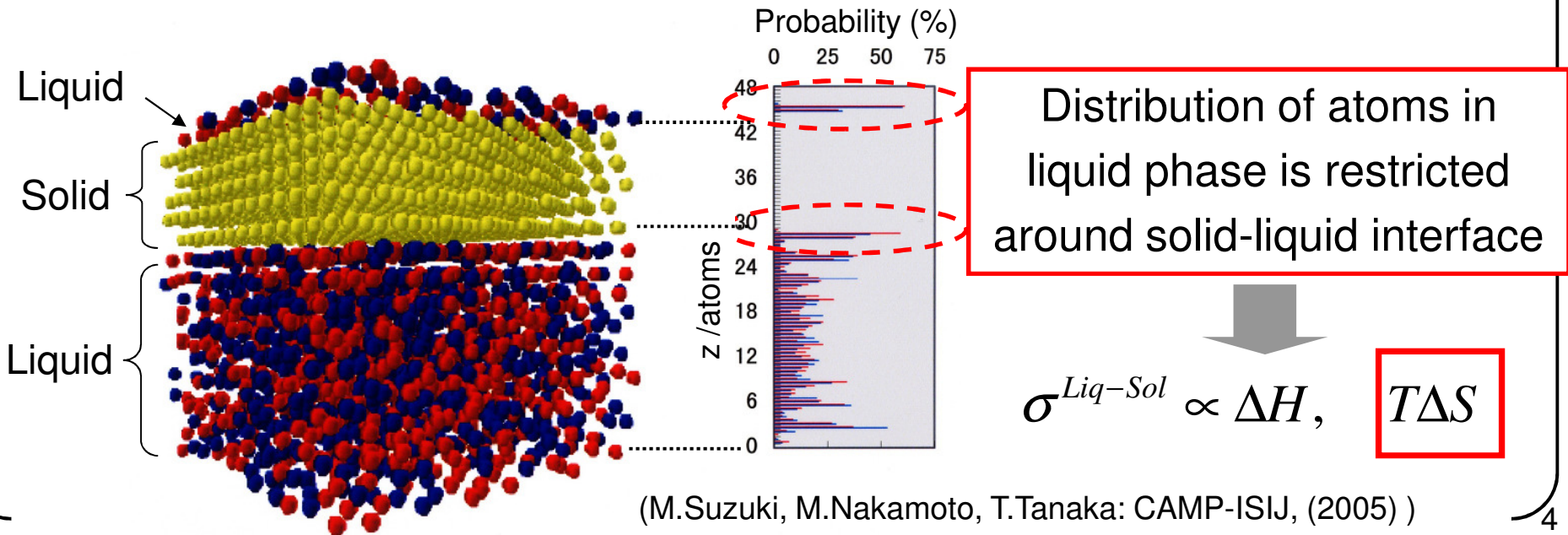
Evaluation of Solid-liquid Interfacial Energies of Alloys based on Thermodynamic Properties

$$\Delta H$$

Not only the contribution from enthalpy, we consider the contribution from **entropy change** onto solid-liquid interfacial energy

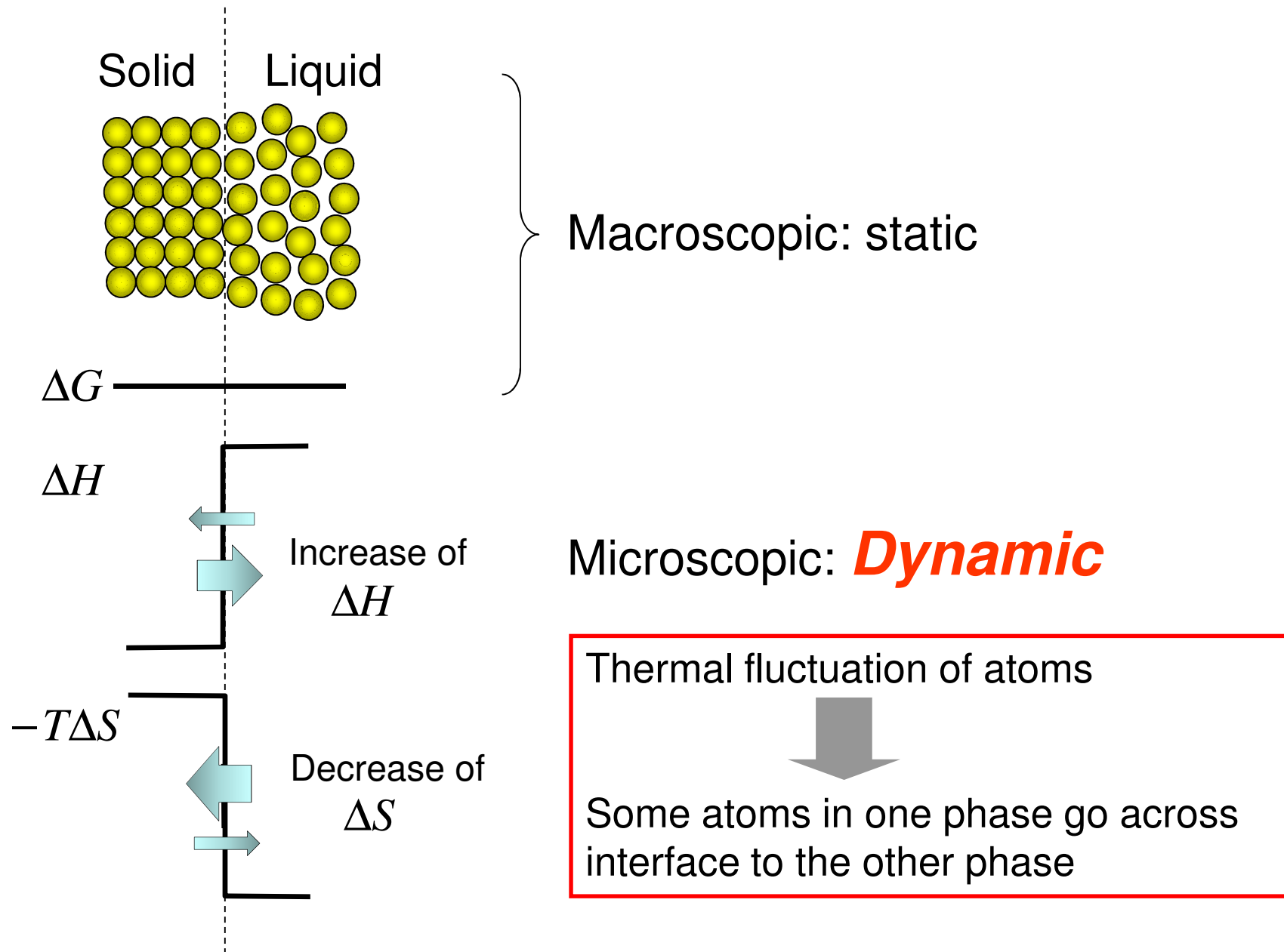
$$T\Delta S$$

Ex. Molecular dynamics calculation of solid-liquid interface:



(M.Suzuki, M.Nakamoto, T.Tanaka: CAMP-ISIJ, (2005))

Phase equilibrium between solid and liquid metals:



Solid Interfacial layers *Liquid*

$G^{Solid} = G^{Liquid}$

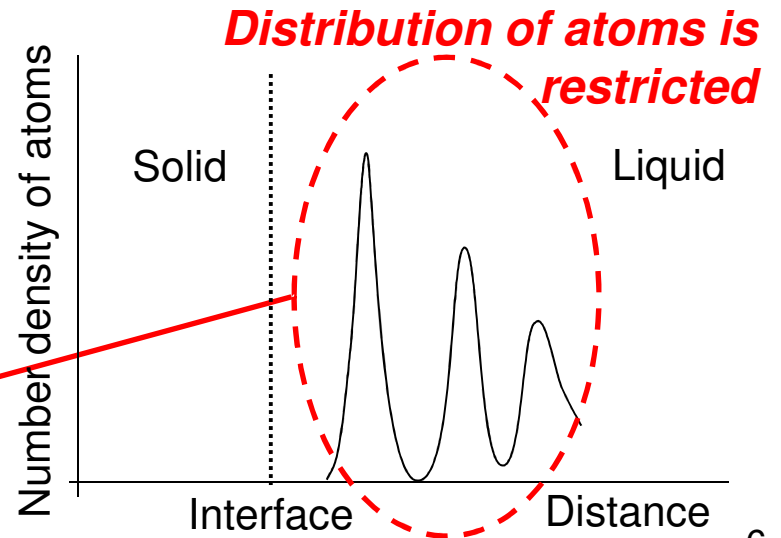
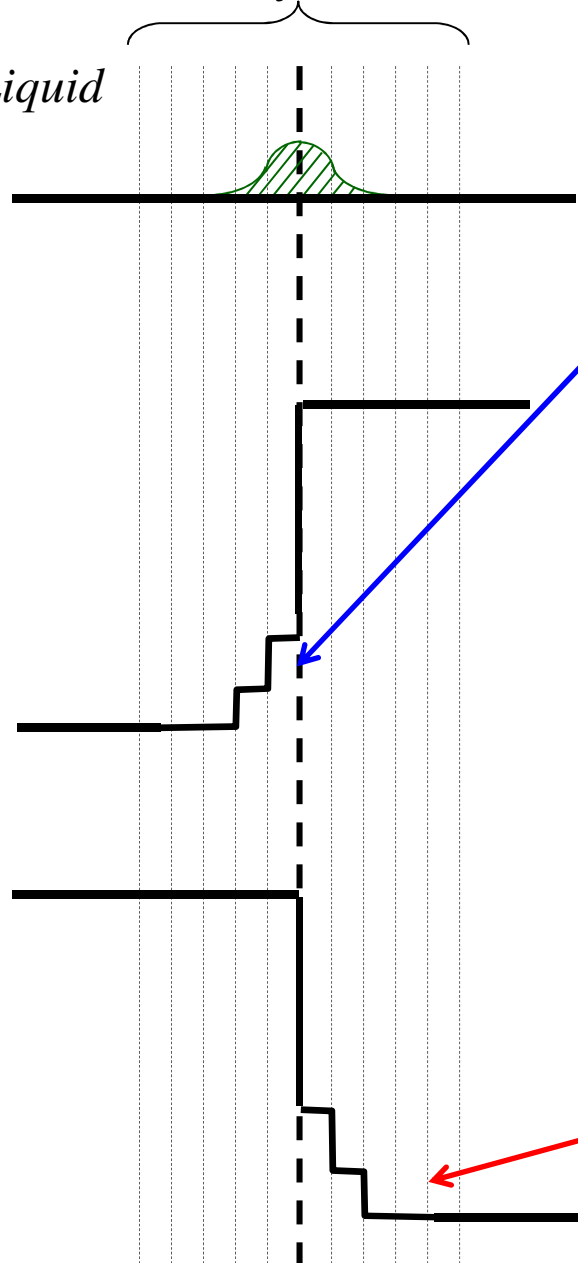
ΔG_f

Atoms in solid phase around interface may have higher energies than those in bulk

ΔH_f

Excess enthalpy and entropy may be generated at interface

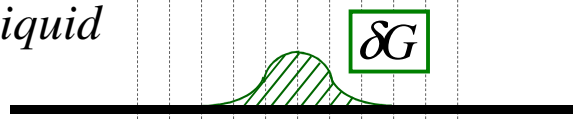
$-T \cdot \Delta S_f$



Solid Interfacial layers Liquid

1 2 N

$$G^{Solid} = G^{Liquid}$$



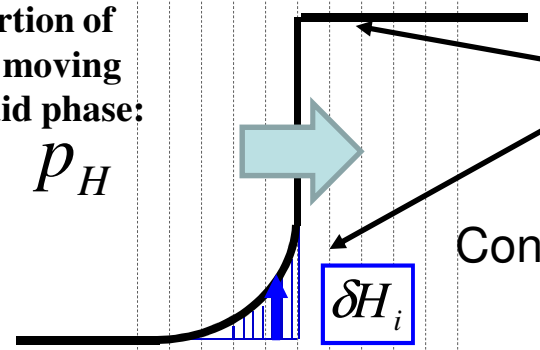
Energetic barrier of $\delta G (= \delta H \text{ or } T\delta S)$ for atoms to go across interfacial area
 $\longrightarrow \sigma^{Liq-Sol} \cdot A$

$$\Delta G_f$$

Proportion of atoms moving to liquid phase:

$$\Delta H_f$$

p_H



$$\delta H = \sum_i \delta H_i \propto \Delta H_f > 0$$

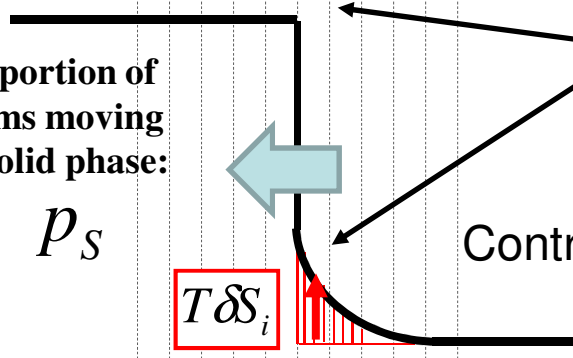
i Layer: 1 ~ N

Contribution from **excess enthalpy** to $\sigma^{Liq-Sol} \cdot A$
 $= \delta H \cdot p_H$

Proportion of atoms moving to solid phase:

$$-T \cdot \Delta S_f$$

p_S



$$T\delta S = T(\sum_i \delta S_i) \propto T \cdot \Delta S_f > 0$$

i Layer: 1 ~ N

Contribution from **excess entropy** to $\sigma^{Liq-Sol} \cdot A$
 $= T\delta S \cdot p_S$

Present Model to Evaluate Solid-liquid Interfacial Energy of *Pure Metals*

$$\sigma^{Liq-Sol} = \frac{1}{A} \cdot \frac{\alpha}{2} (\Delta H^{Melting} + \beta \cdot T \cdot \Delta S^{Melting})$$

1. Alpha = Ratio of coordination numbers, $Z^{Interface} / Z^{Bulk,Solid}$
and it depends on **crystal structure and plane of solid phase**
(based on Granasy et al.)

$$\alpha_{min} \Rightarrow \text{FCC:0.458, HCP : 0.458, BCC : 0.445, DC : 0.289}$$

$$\alpha_{max} \Rightarrow \text{FCC:0.592, HCP : 0.582, BCC : 0.630, DC : 0.500}$$

$$\alpha_{ave} \Rightarrow \text{FCC:0.561, HCP : 0.561, BCC : 0.546, DC : 0.433}$$

2. Beta = Ratio of contribution from $\Delta H^{Melting}$ and $T \Delta S^{Melting}$
onto interfacial energy (determined from expe $\sigma^{Liq-Sol}$ data)

Calculated Results of Solid-liquid Interfacial Energy of Pure Metals

$$\sigma^{Liq-Sol} = \frac{1}{A} \cdot \frac{\alpha}{2} (\Delta H^{Melting} + \beta \cdot T \cdot \Delta S^{Melting})$$

$$(\beta = 0.8)$$

Crystal structure	$\Delta H^{Melting}$ [kJ/mol]	Molar volume [cm ³ /mol]	Interfacial area [m ² /mol]	Melting point [K]	$\Delta S^{Melting}$ [J/mol·K]	$\sigma^{Liq-Sol}(\text{Calc})$ [mJ/m ²]	$\sigma^{Liq-Sol}(\text{Expe})$ [mJ/m ²]
Ag	11.09	11.6	43220.4	1234	9.0	136.0	140.9
Ag	11.09	11.6	43220.4	1234	9.0	136.0	126.0
Al	10.46	11.3	42472.0	933	11.2	130.6	132.0
Al	10.46	11.3	42472.0	933	11.2	130.6	102.0
Au	12.76	11.3	42472.0	1336	9.6	159.3	146.1
Au	12.76	11.3	42472.0	1336	9.6	159.3	132.0
Co	15.48	7.6	32603.1	1765	8.8	251.7	263.9
Co	15.48	7.6	32603.1	1765	8.8	251.7	234.0
Cu	13	7.94	33568.4	1356	9.6	205.3	197.1
Cu	13	7.94	33568.4	1356	9.6	205.3	177.0
Ni	17.15	7.43	32115.1	1728	9.9	283.1	284.6
Ni	17.15	7.43	32115.1	1728	9.9	283.1	255.0

Molar volume data for solid metals are used to estimate interfacial area:

$$A = \left(\frac{V_{m,solid}}{N_A} \right)^{2/3} \cdot N_A$$

FactSage and the latest thermodynamic databases for alloy systems are used to evaluate $\Delta H^{Melting}$ and $\Delta S^{Melting}$ ($= \Delta H^{Melting} / T_m$)

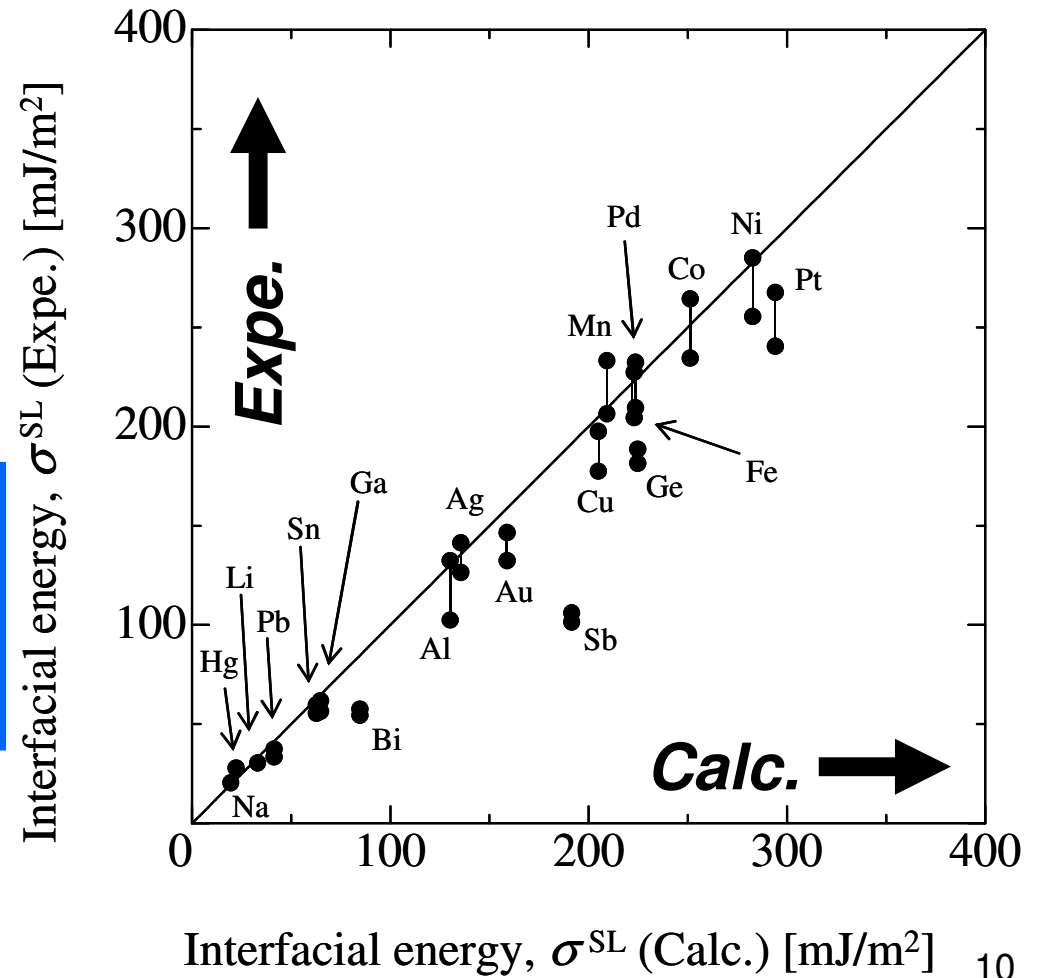
Comparison between Calc and Expe Solid-liquid Interfacial Energies of Pure Metals

$$\sigma^{Liq-Sol} = \frac{1}{A} \cdot \frac{\alpha}{2} (\Delta H^{Melting} + \beta \cdot T \cdot \Delta S^{Melting})$$

$$(\beta = 0.8)$$

Expe. data are basically provided using Gibbs-Thompson theory (Nucleation frequency)

Good agreements are obtained when $\beta = 0.8$ is assumed

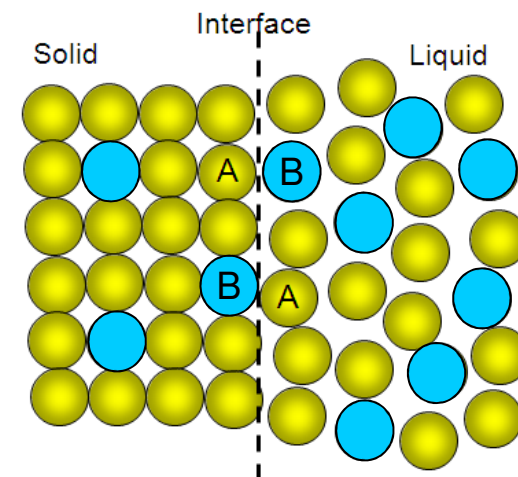


Present Model to Estimate Solid-liquid Interfacial Energy of Alloys

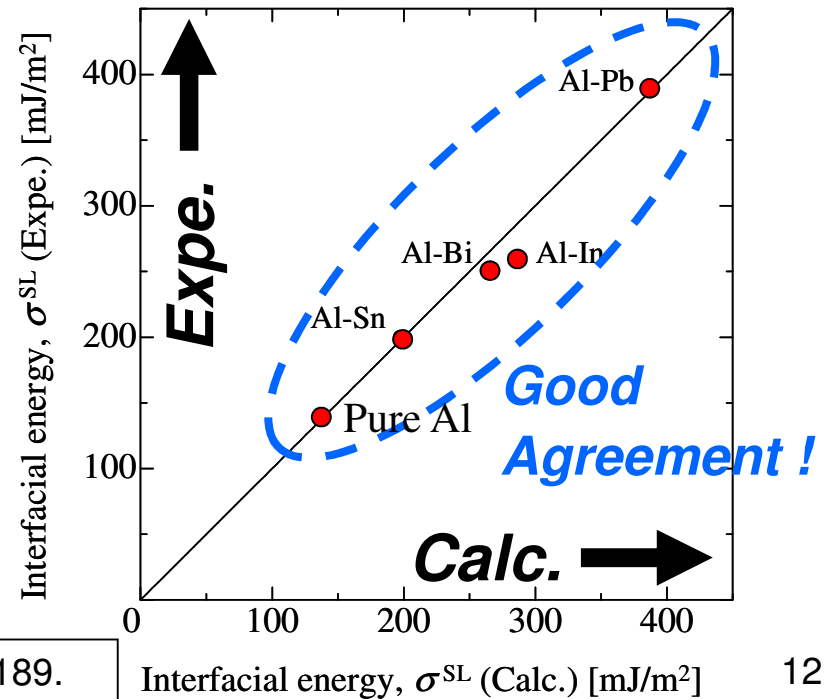
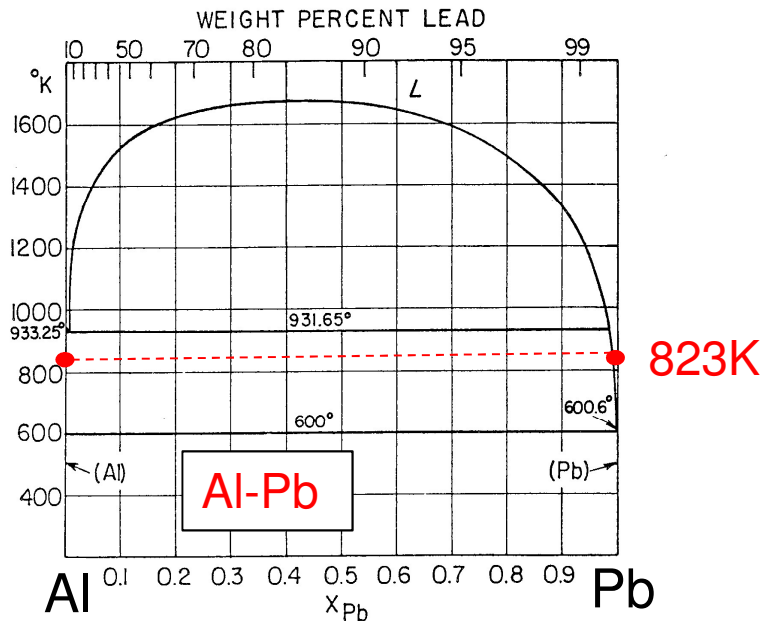
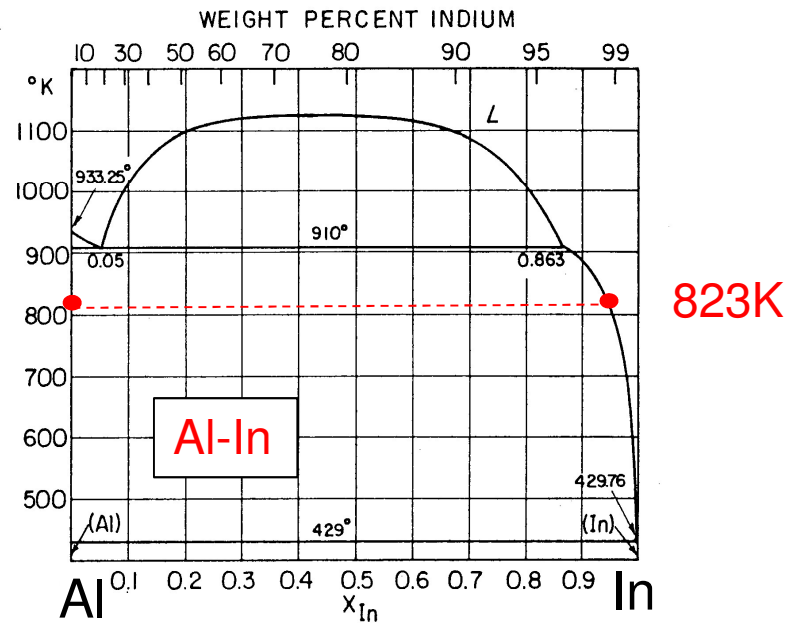
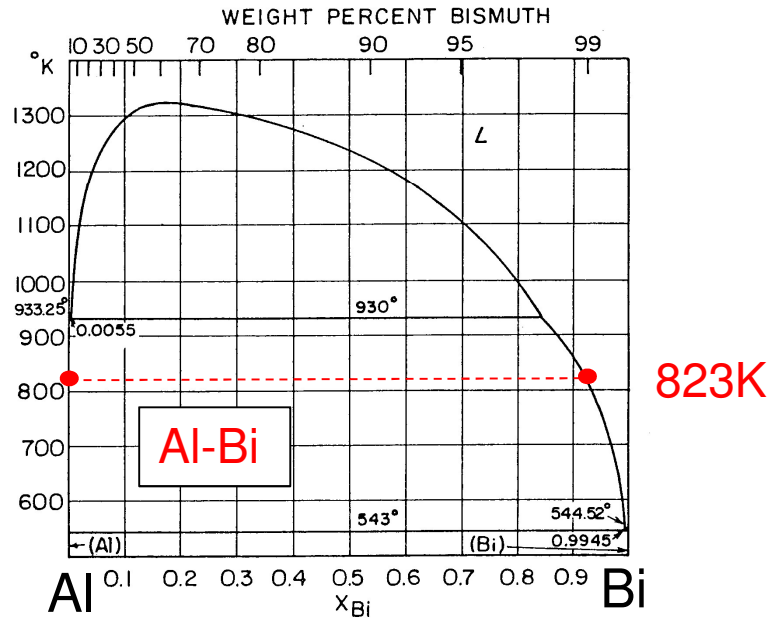
$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \left\{ \underbrace{(x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B})}_{\Delta H^{Melting}} + T \cdot \underbrace{(x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B})}_{T \Delta S^{Melting}} \right\} \cdot \beta + H^{Ex}$$

1. Additive equation is assumed to estimate the contributions from $\Delta H^{Melting}$ and $T \Delta S^{Melting}$ as functions of composition of liquid phase
2. Contribution from excess energy, H^{Ex} due to interactions between different kinds of atoms across the interface, is introduced

$$\begin{aligned} \Delta H_{Alloy}^{Excess} &= \frac{1}{2} (\Omega_{AB}^{Interface} \cdot x_A^L \cdot x_B^S + \Omega_{AB}^{Interface} \cdot x_A^S \cdot x_B^L) \\ &\quad - \frac{1}{2} (\Omega_{AB}^{Liquid} \cdot x_A^L \cdot x_B^L + \Omega_{AB}^{Solid} \cdot x_A^S \cdot x_B^S) \\ \left(\Omega_{AB}^{Interface} &= \frac{1}{2} (\Omega_{AB}^{Liquid} + \Omega_{AB}^{Solid}) \right) \end{aligned}$$

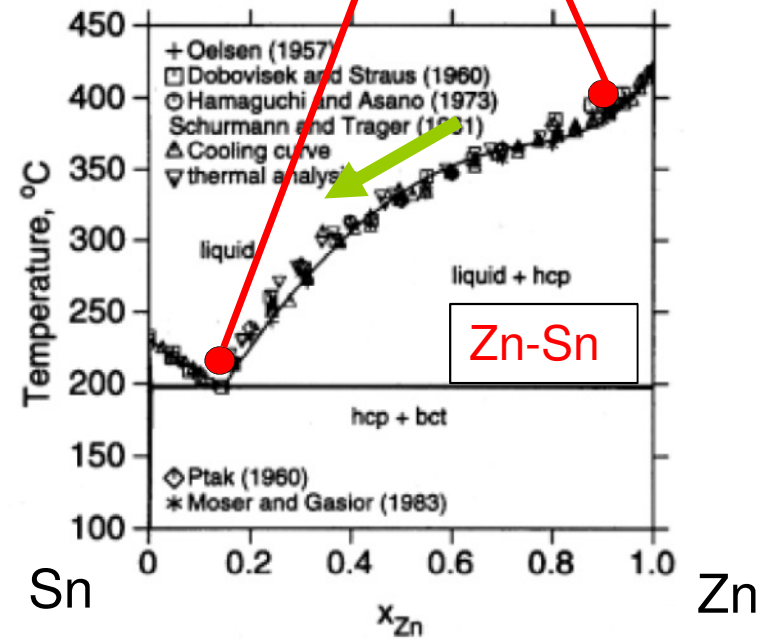
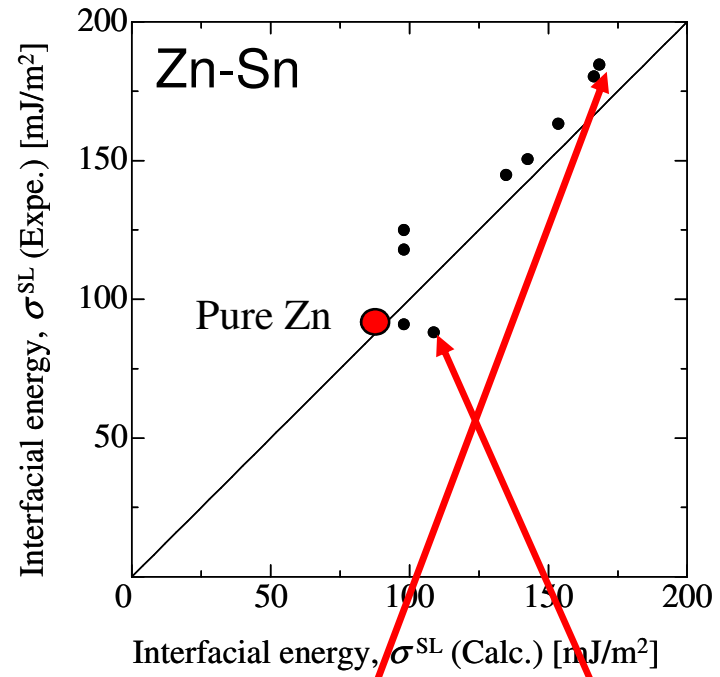
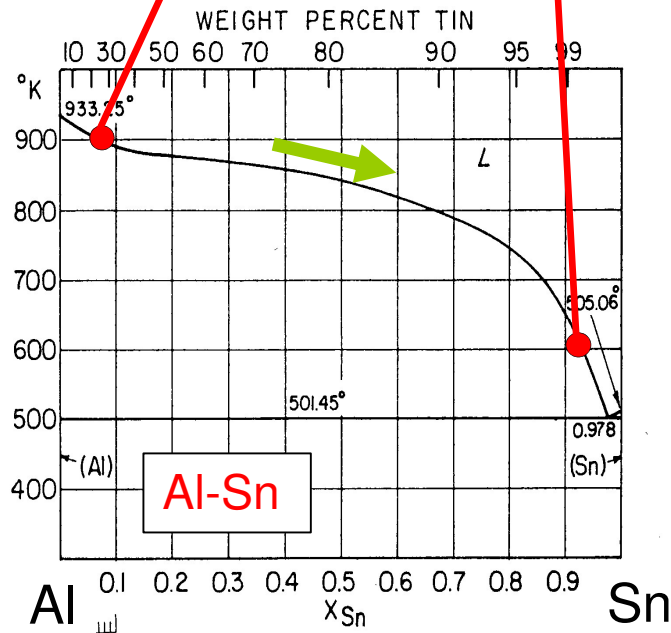
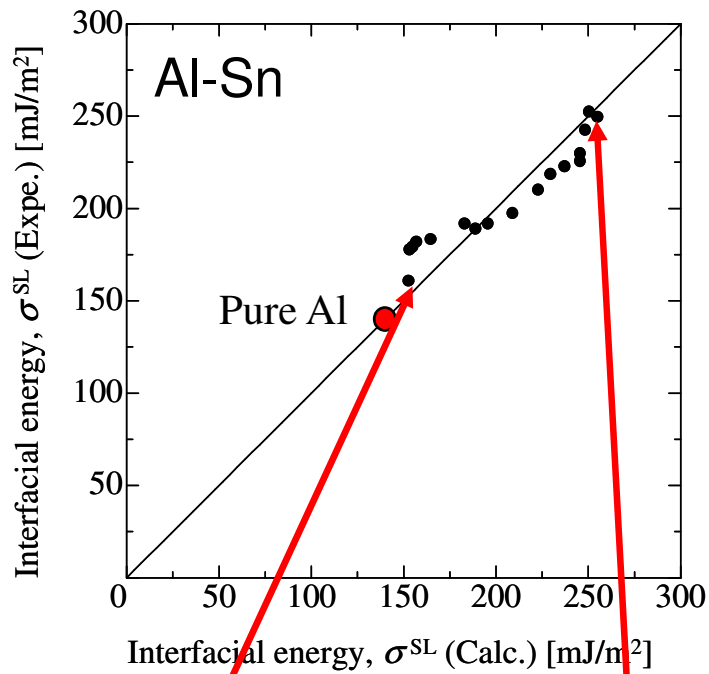


Solid-liquid interfacial energy of Al-based alloys at 823 K



Expe data: N.Eustathopoulos: Inter. Metals Review, **28**(1983), 189.

Composition dependence of solid-liquid interfacial energy



Solid-liquid Interfacial Energy of Ferrous Alloys

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \{ (x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B}) + T \cdot (x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B}) \cdot \beta + H^{Ex}$$

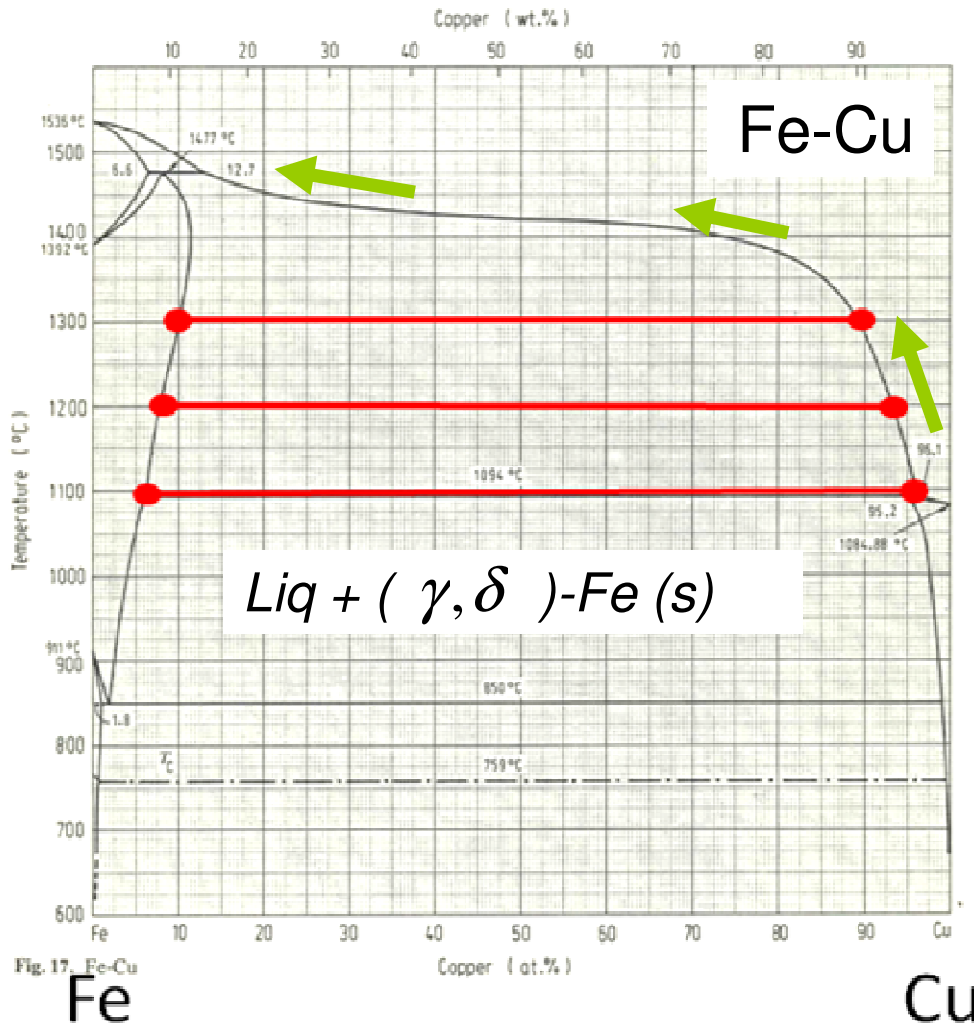
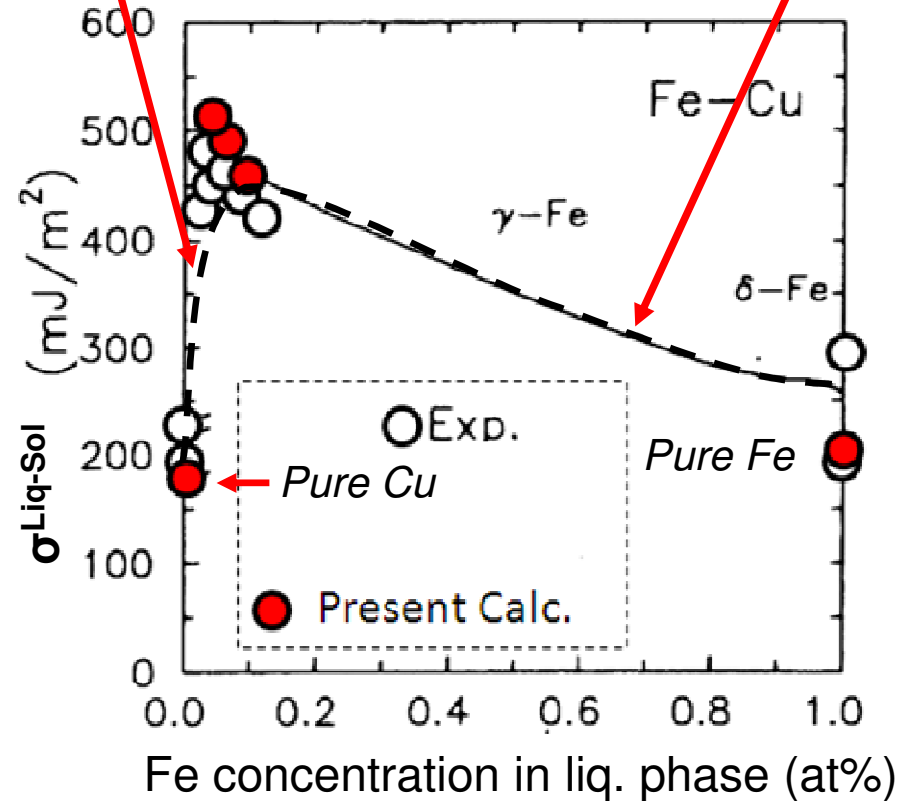


Fig. 17. Fe-Cu



Expe data: L. Granasy & T. Tegze :Mat.Sci. Forum, 77 (1991), 243.

Contribution from Enthalpy and Entropy of Fusion onto Solid-liquid Interfacial Energy in Other Proposed Models

$$\sigma^{Liq-Sol} = \frac{1}{A} (a \cdot \Delta H^{Melting} + b \cdot T \cdot \Delta S^{Melting})$$

Author	Contributions		Application to alloys
	$\Delta H^{Melting}$	$T \Delta S^{Melting}$	
• Skapski (1956)	>90	<10	
• Zadumkin (1962)	100	0	
• Ewing (1971)	50	50	
• Eustathopoulos et al. (1973~)	100	0	○
• Spaepen (1975~)	0	100	
• Waseda et al. (1978)	50	50	
• Miedema et al. (1979)	25	75	
• Warren (1980)	100	0	○
• Granasy et al. (1991~)	50	50	○
• Battezzati (2000)	65	35	
• Kaptay (2001~)	50	50	
• Digilov (2002~)	0	100	
• Jones (2002)	50	50	
• Shimizu et al. (2005~)	100	0	○

Conclusions

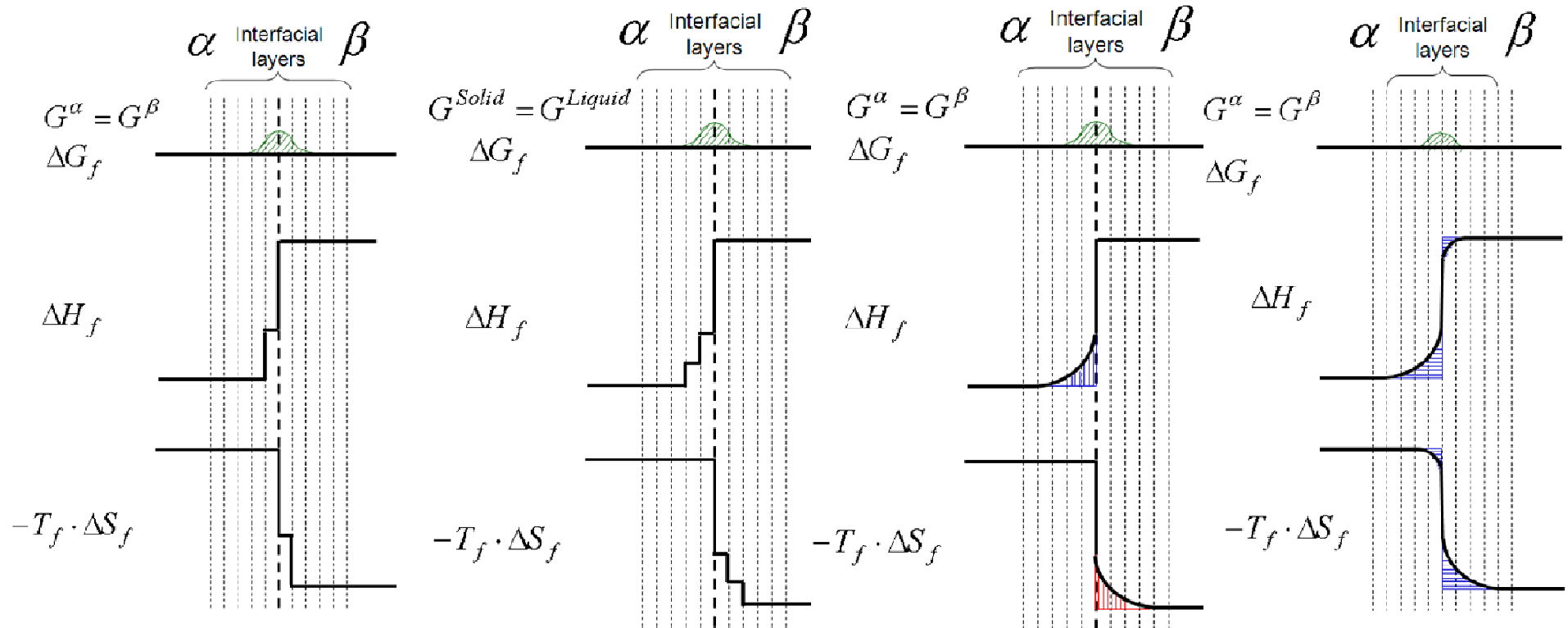
A model was proposed to estimate **solid-liquid interfacial energy of alloy systems** using **thermodynamic properties**.

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \left\{ \underbrace{(x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B})}_{\Delta H^{Melting}} + T \cdot \underbrace{(x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B})}_{T \Delta S^{Melting}} \right\} \cdot \beta + H^{Ex}$$

The present model contains the contribution from both **enthalpy** and **entropy of fusion**.

The present model estimates solid-liquid interfacial energies of alloys **in good agreements with existing experimental data**.

$$\sigma^{\alpha-\beta} \cdot A = \left(G - \left(G^\alpha + G^\beta \right) \right)$$



1. Solid-liquid interfacial energy basically has **positive temperature dependence**, which results in **negative dependence of solute composition**.
2. However, if solute element A has very high **latent heat and entropy of fusion**, interfacial energy between pure A solid and A-based alloy **increases as concentration of A increases**.
3. For those systems with **large positive interactions**, interfacial energy **increases as solute concentration of liquid alloy increases**.

Calculated Results of Solid-liquid Interfacial Energy of Pure Metals

	Crystal structure	Latent heat [kJ]	Molar volume ³	Molar area	Melting point [K]	Entropy of fusion	$\sigma^{Liq-Sol}$ (Calc)	$\sigma^{Liq-Sol}$ (Expe)
Ag	fcc	11.09	11.6	43220.4	1234	9.0	136.0	140.9
Ag	fcc	11.09	11.6	43220.4	1234	9.0	136.0	126.0
Al	fcc	10.46	11.3	42472.0	933	11.2	130.6	132.0
Al	fcc	10.46	11.3	42472.0	933	11.2	130.6	102.0
Au	fcc	12.76	11.3	42472.0	1336	9.6	159.3	146.1
Au	fcc	12.76	11.3	42472.0	1336	9.6	159.3	132.0
Co	fcc	15.48	7.6	32603.1	1765	8.8	251.7	263.9
Co	fcc	15.48	7.6	32603.1	1765	8.8	251.7	234.0
Cu	fcc	13	7.94	33568.4	1356	9.6	205.3	197.1
Cu	fcc	13	7.94	33568.4	1356	9.6	205.3	177.0
Ni	fcc	17.15	7.43	32115.1	1728	9.9	283.1	284.6
Ni	fcc	17.15	7.43	32115.1	1728	9.9	283.1	255.0
Pb	fcc	4.81	19.42	60937.3	601	8.0	41.8	37.0
Pb	fcc	4.81	19.42	60937.3	601	8.0	41.8	33.0
Pd	fcc	16.7	10.14	39513.2	1828	9.1	224.1	231.9
Pd	fcc	16.7	10.14	39513.2	1828	9.1	224.1	209.0
Pt	fcc	22.2	10.31	39953.6	2047	10.8	294.6	267.1
Pt	fcc	22.2	10.31	39953.6	2047	10.8	294.6	240.0
Fe	bcc	13.77	7.94	33568.4	1808	7.6	223.4	226.9
Fe	bcc	13.77	7.94	33568.4	1808	7.6	223.4	204.0
Li	bcc	2.93	13.4	47583.2	452	6.5	33.5	30.0
Mn	bcc	14.6	9.54	37938.7	1517	9.6	209.6	232.8
Mn	bcc	14.6	9.54	37938.7	1517	9.6	209.6	206.0
Na	bcc	2.64	24.8	71727.4	371	7.1	20.0	20.0
Sb	A-7	39.7	18.8	59633.3	904	43.9	191.9	105.6
Sb	A-7	39.7	18.8	59633.3	904	43.9	191.9	101.0
Sn	A-5	7.07	17	55763.5	505	14.0	63.2	59.3
Sn	A-5	7.07	17	55763.5	505	14.0	63.2	55.0
Bi	A-7	10.88	20.8	63791.0	544	20.0	85.1	57.1
Bi	A-7	10.88	20.8	63791.0	544	20.0	85.1	54.0
Ga	A-11	5.59	11.4	42722.2	303	18.4	65.3	61.3
Ga	A-11	5.59	11.4	42722.2	303	18.4	65.3	56.0
Ge	DC	36.8	13.2	47108.5	1231	29.9	225.2	188.2
Ge	DC	36.8	13.2	47108.5	1231	29.9	225.2	181.0
Hg	A-10	2.301	14.65	50498.2	234	9.8	22.7	27.5

	温度 (K)	液相線 モル分率	固相線 モル分率	界面エネルギー mN/m
Fe-Al	1808	0.000	0.000	212
	1773	0.265	0.240	177
	1723	0.350	0.310	163
	1673	0.410	0.375	155
Fe-Si	1808	0.000	0.000	212
	1773	0.050	0.030	203
	1723	0.110	0.075	192
	1673	0.150	0.120	186
	1573	0.225	0.180	172
Fe-Ni	1808	0.000	0.000	212
	1793	0.040	0.028	214
Fe-Co	1808	0.000	0.000	212
	1773	0.160	0.120	201
Fe-Cu	1808	0.000	0.000	212
	1798	0.050	0.025	209
	1773	0.090	0.050	207
	1573	0.900	0.100	467
	1473	0.930	0.075	498
	1373	0.960	0.060	524
Fe-Cr	1808	0.000	0.000	212
	1793	0.125	0.050	228
Fe-Mn	1808	0.000	0.000	212
	1773	0.070	0.045	211
	1746	0.125	0.090	212
Fe-Mo	1808	0.000	0.000	212
	1773	0.080	0.060	230

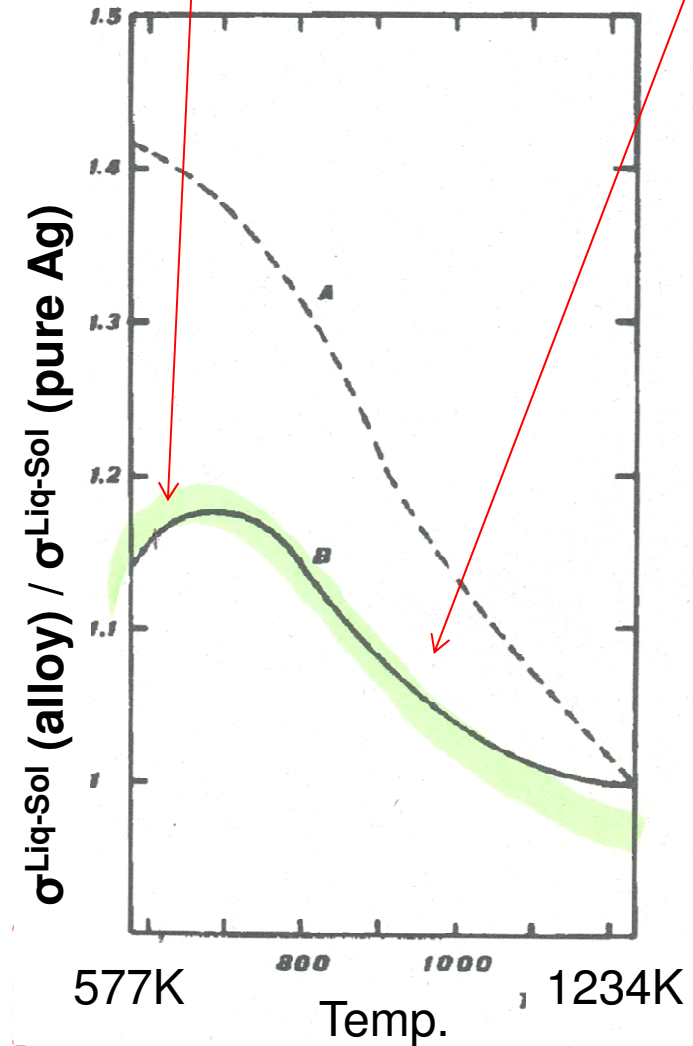
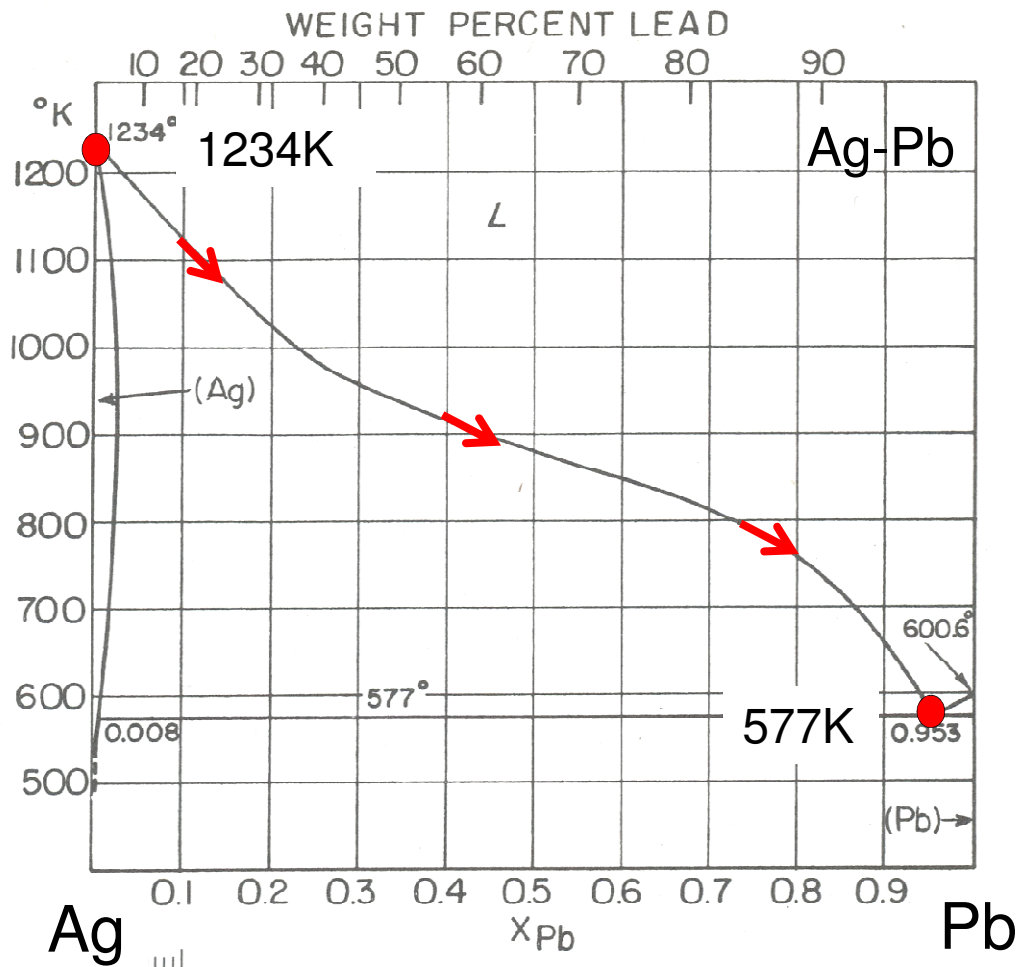
Liq-
yFe

	温度 (K)	液相線 モル分率	固相線 モル分率	界面エネルギー mN/m
Fe-Zr	1808	0.000	0.000	212
	1773	0.025	0.005	214
	1723	0.050	0.005	215
	1628	0.080	0.005	212
Fe-Ti	1808	0.000	0.000	212
	1773	0.025	0.010	211
	1723	0.055	0.025	210
	1673	0.090	0.045	209
	1573	0.155	0.090	205
Fe-Nb	1808	0.000	0.000	212
	1673	0.090	0.025	226
Fe-Ta	1808	0.000	0.000	212
	1723	0.070	0.025	221
Fe-V	1808	0.000	0.000	212
	1793	0.090	0.050	215
	1773	0.175	0.110	217
Fe-W	1808	0.000	0.000	212
	1803	0.044	0.040	221

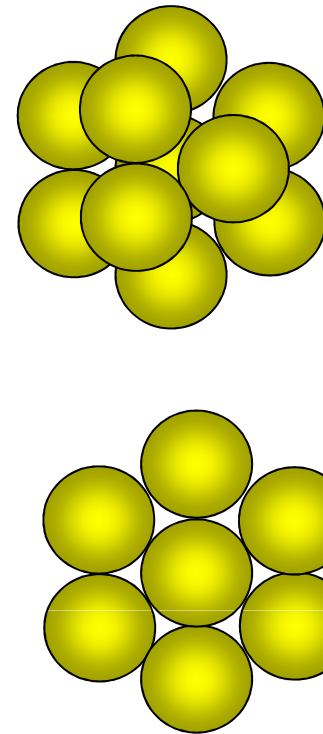
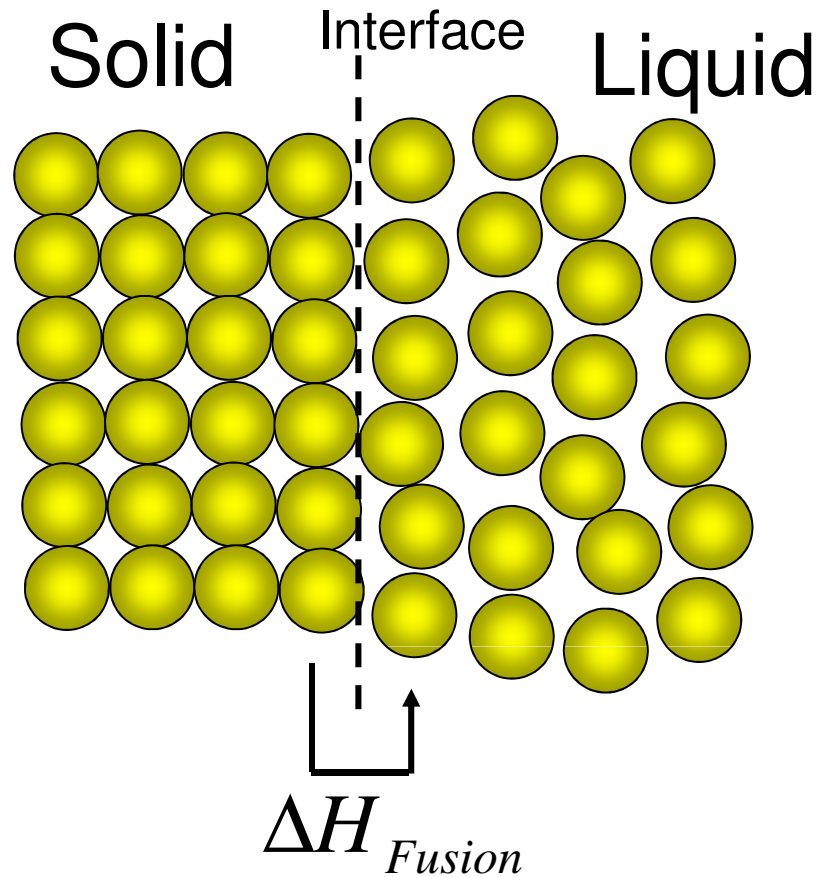
**Solid-liquid interfacial energy
of Fe-based alloys**

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \left\{ (x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B}) + T \cdot (x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B}) \cdot \beta + H^{Ex} \right\}$$

Composition dependence of solid-liquid interfacial energy



Passerone et al.(1982)



Number of nearest neighbor atoms around one atom: 12

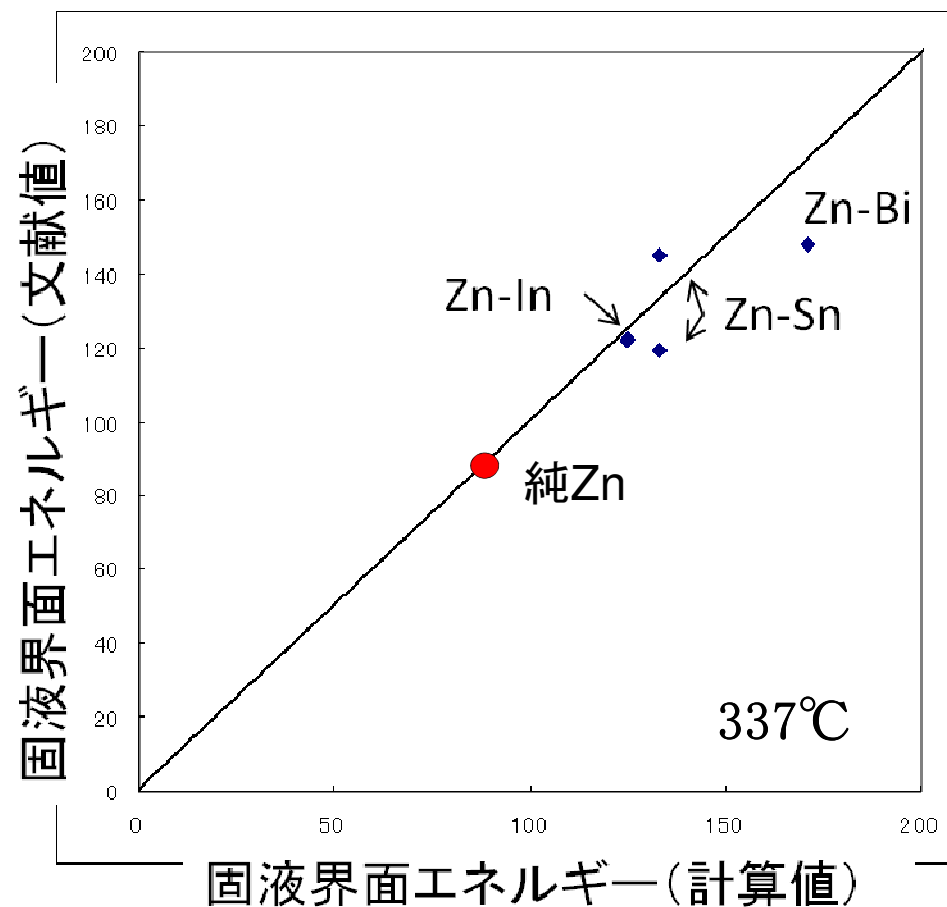
6 in parallel,
3 in lower,
3 in upper layer



If 3 atoms in upper layer are removed, interface (or surface) is obtained

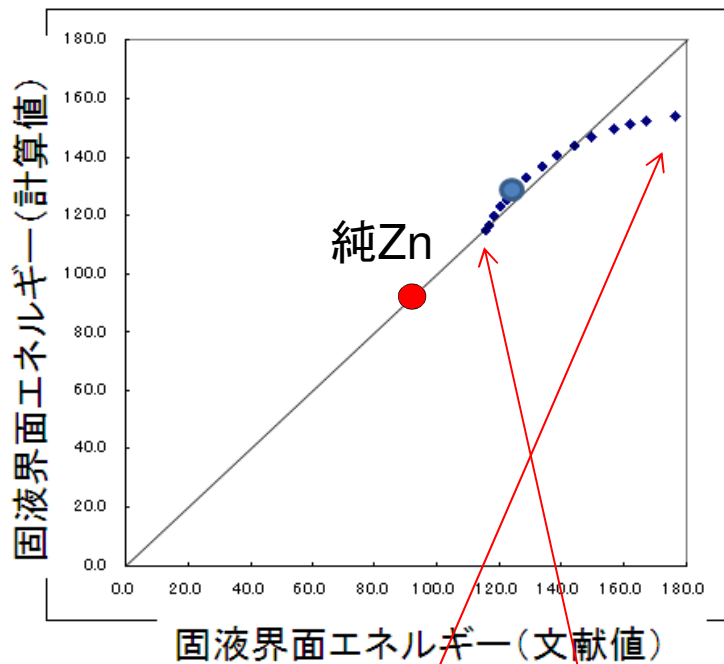
$$\sigma^{Liq-Sol} = \frac{1}{A} \cdot \left(\frac{3}{12} \cdot \Delta H_{Fusion} \right) = \frac{1}{A} \cdot \left(\frac{1}{4} \cdot \Delta H_{Fusion} \right) \Leftrightarrow \left(\frac{1}{4} \cdot \Delta H_{Fusion} + \frac{1}{4} \cdot ? \right)$$

Zn系合金

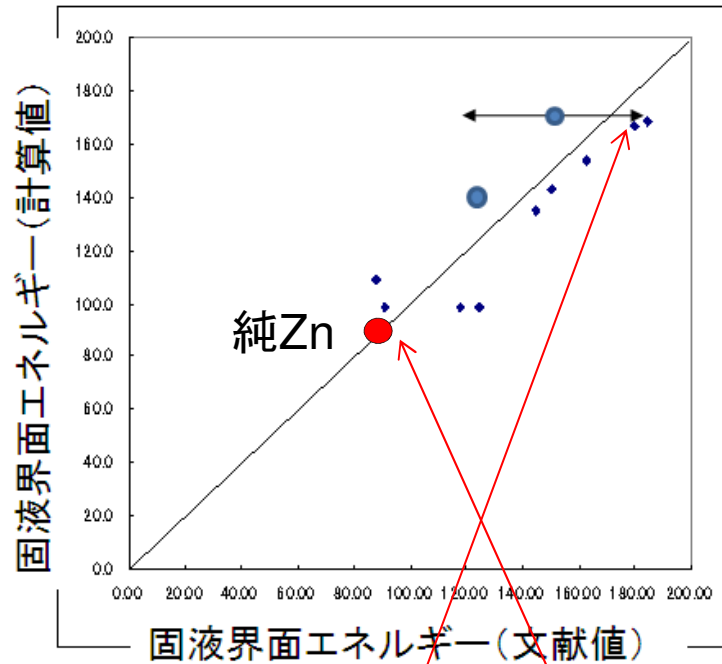
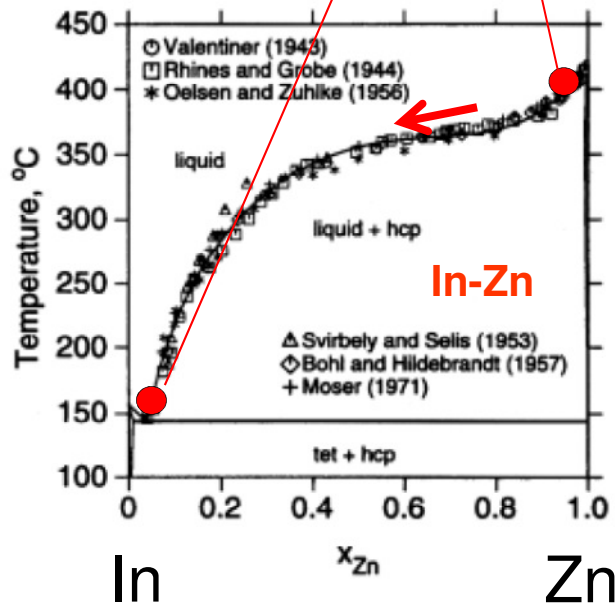


Zn系合金の固液界面エネルギー

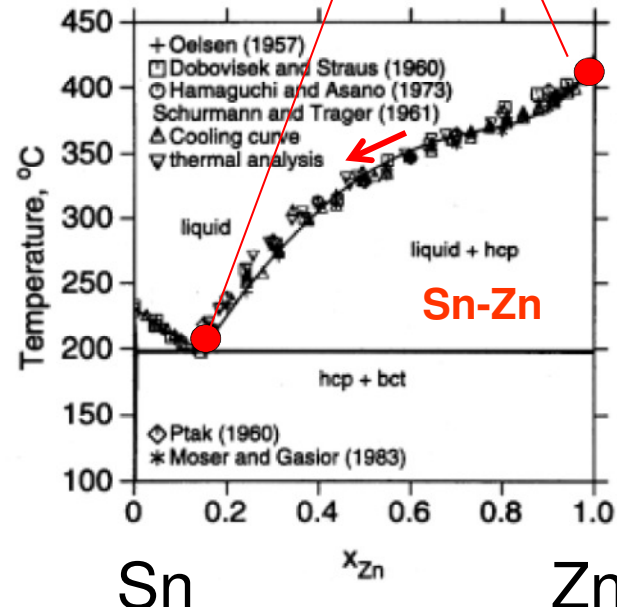
文献値 : N.Eustathopoulos : Inter. Metals Review, Vol.28 (1983), pp.189-210から検索・引用



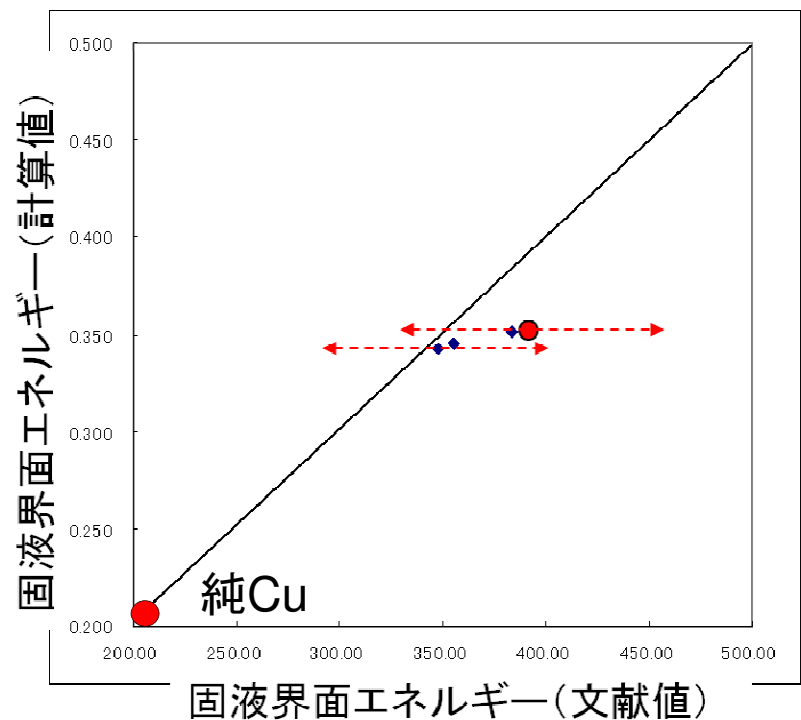
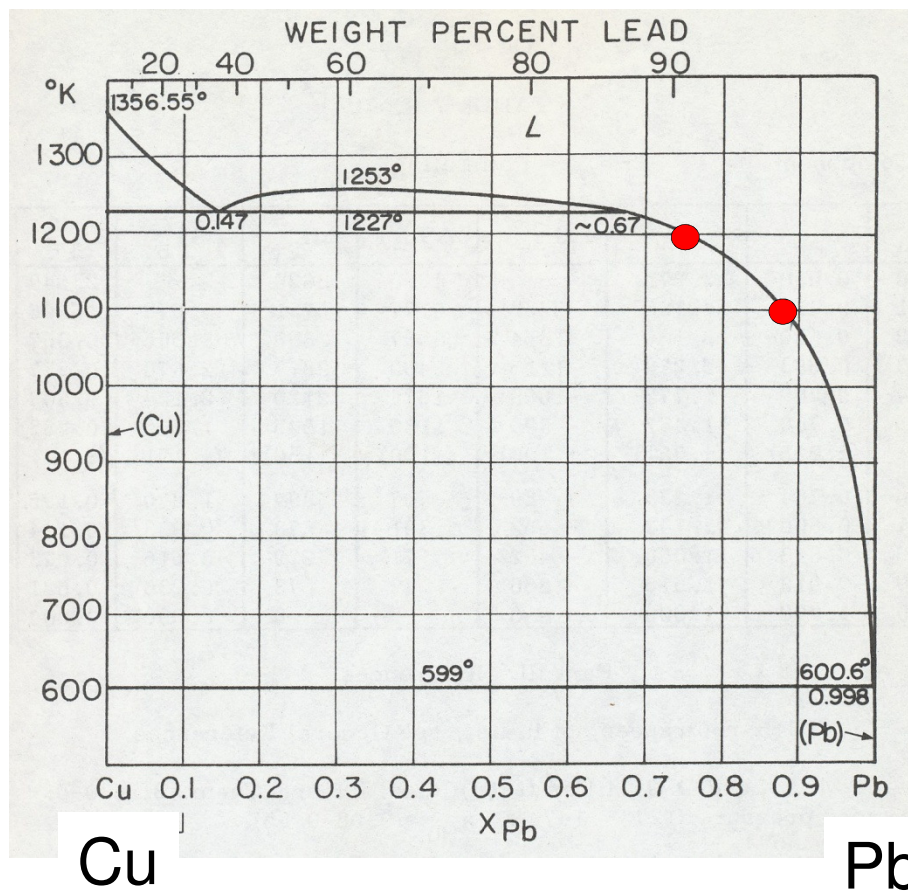
Zn-In系合金の固液界面エネルギー



Zn-Sn系合金の固液界面エネルギー



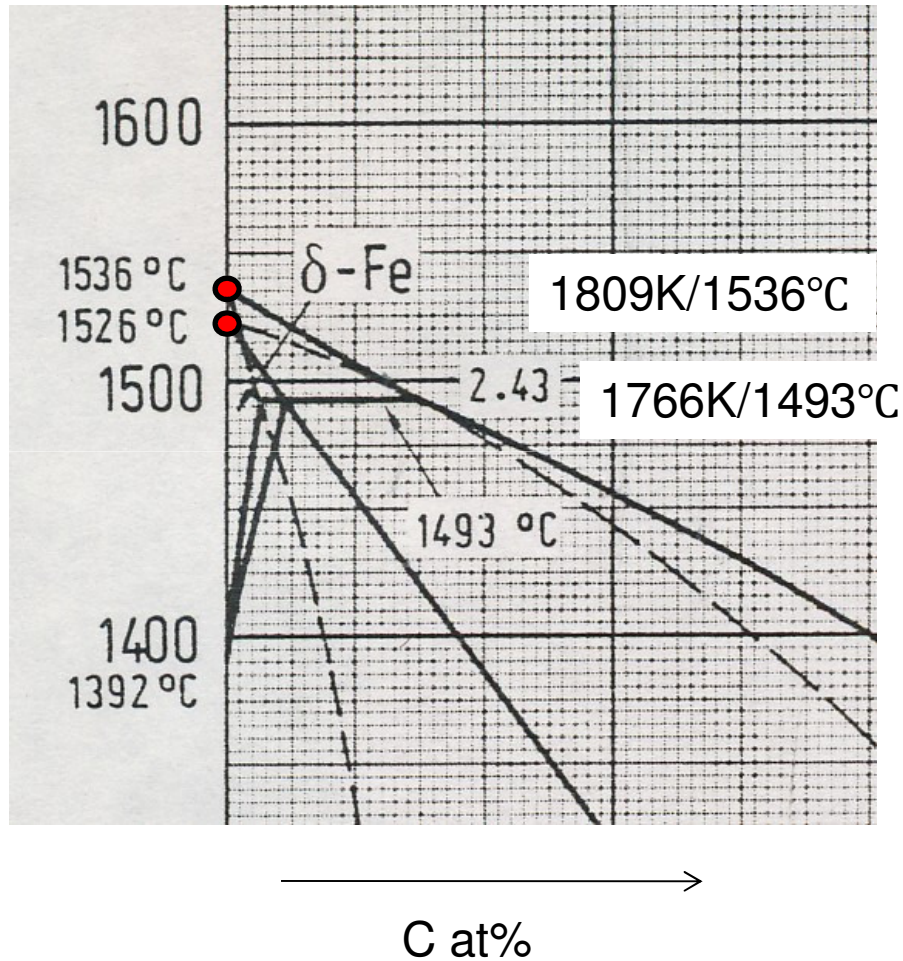
文献値:
N.Eustathopoulos: Inter.
Metals Review,
Vol.28 (1983),
pp.189-210か
ら検索・引用



Cu-Pb系合金の固液界面エネルギー

文献値 : N.Eustathopoulos : Inter. Metals Review, Vol.28 (1983), pp.189-210から検索・引用

Fe-C2元系合金の 固液界面エネルギー

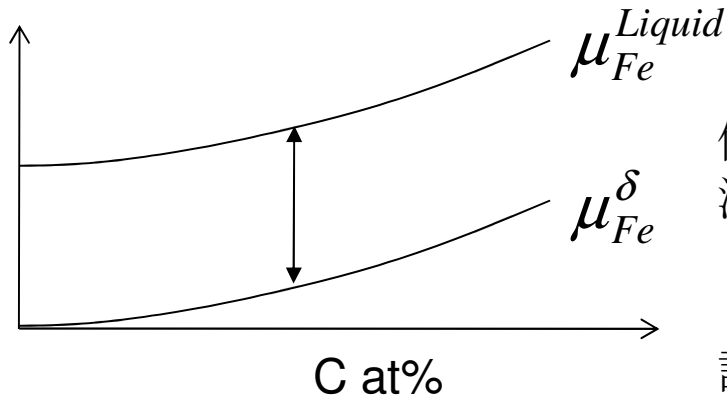


$$\begin{aligned} \sigma_{Fe}^{L-BCC, Pure} &= \frac{1}{A} \cdot \frac{\alpha_{BCC}}{2} \cdot (\Delta H_{m, Fe}^{L-BCC} + T \cdot \Delta S_{m, Fe}^{L-BCC} \cdot \beta) \\ &= 212 \text{ mN / m} \end{aligned}$$

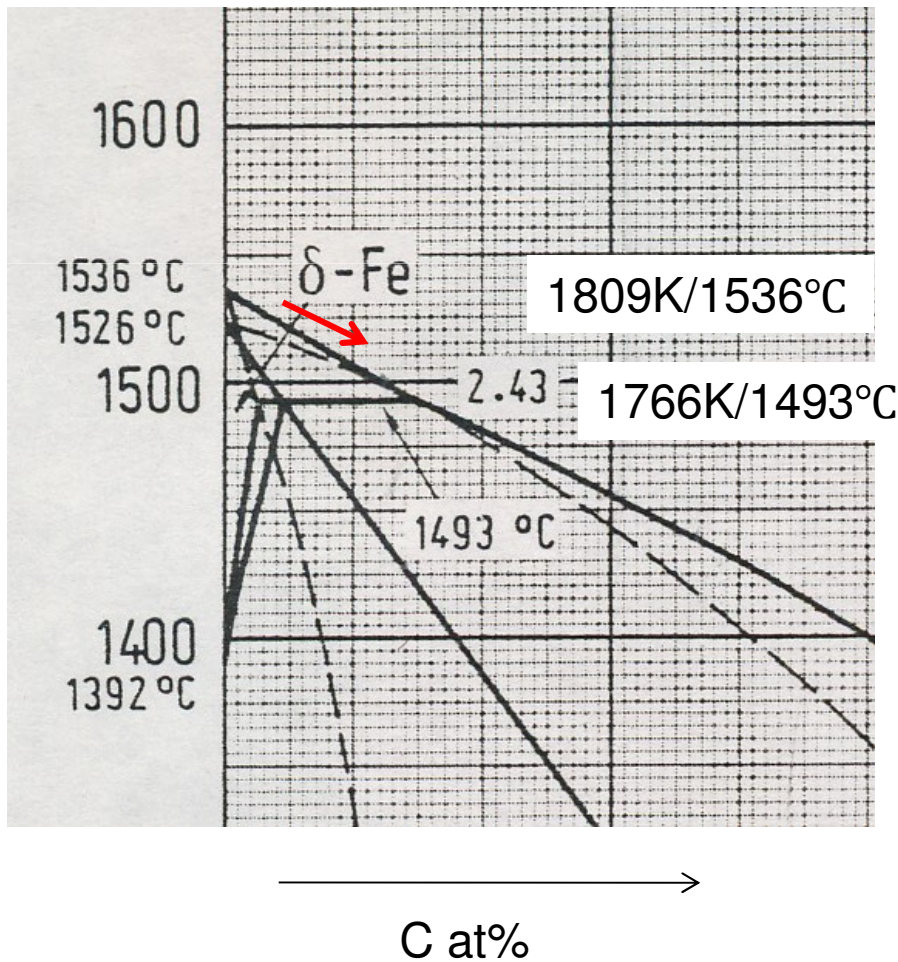
$$\begin{aligned} \sigma_{Fe}^{L-FCC, Pure} &= \frac{1}{A} \cdot \frac{\alpha_{FCC}}{2} \cdot (\Delta H_{m, Fe}^{L-FCC} + T \cdot \Delta S_{m, Fe}^{L-FCC} \cdot \beta) \\ &= 233 \text{ mN / m} \end{aligned}$$

$$\mu_{Fe}^{Liquid} - \mu_{Fe}^{\delta}$$

$$= \Delta H_{Fe}^{Fe-C} - T \cdot \Delta S_{Fe}^{Fe-C}$$



侵入型希薄合金の場合には
溶媒の融解熱、融解のエン
トロピーの溶質濃度変化か
ら
評価

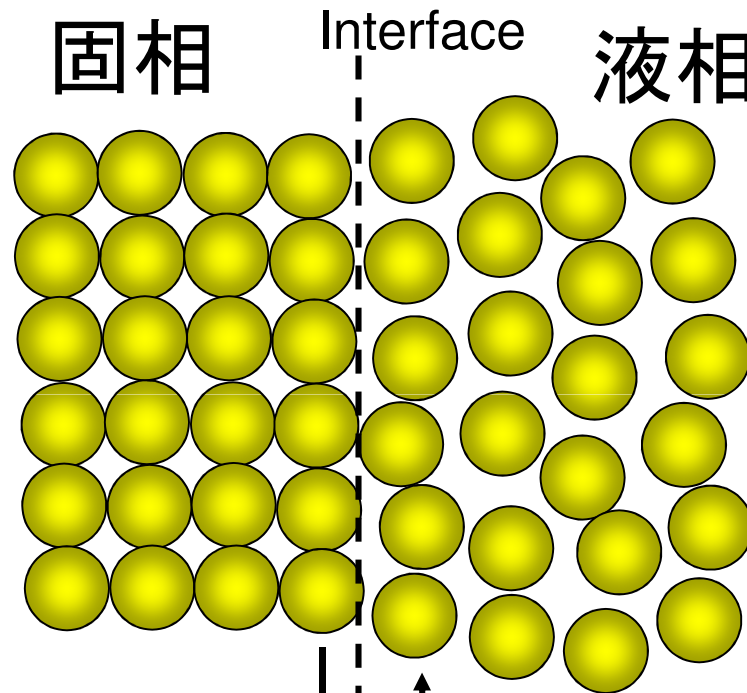


Fe-delta		σ_{Fe-C}^{δ}	
0	1809	212	
0.0122	1788	211	
0.0243	1766	210	

Fe-gamma		σ_{Fe-C}^{γ}	
0	1798.7	233	
0.0122	1783	232	
0.0243	1766	231	
↑	↑		
C at%	Temp./K		

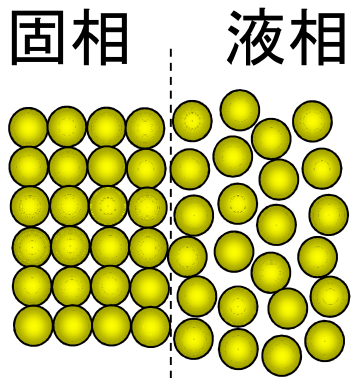
$$\sigma^{Liq-Sol} = \frac{1}{2} \cdot \frac{\Delta H_{Fusion}}{A}$$

なぜ係数は1/2 ???



ΔH_{Fusion}

このエネルギーの差が融解熱であり、その半分だから？



マクロな平衡状態

ΔG

ΔH Eの低い方が安定

抵抗有 (E増加)

$-T\Delta S$

抵抗有 (S低下)

Sの大きい方が安定

原子レベルでは動的な平衡状態

原子は、時折、周りから熱エネルギーを「揺らぎ」として受け取って、界面を越えて隣の相にも移動する。
(ただし、また戻ってくることもある)

固相

液相

界面層

$$G^{Solid} = G^{Liquid}$$

$$\Delta G_f$$

$$\Delta H_f$$

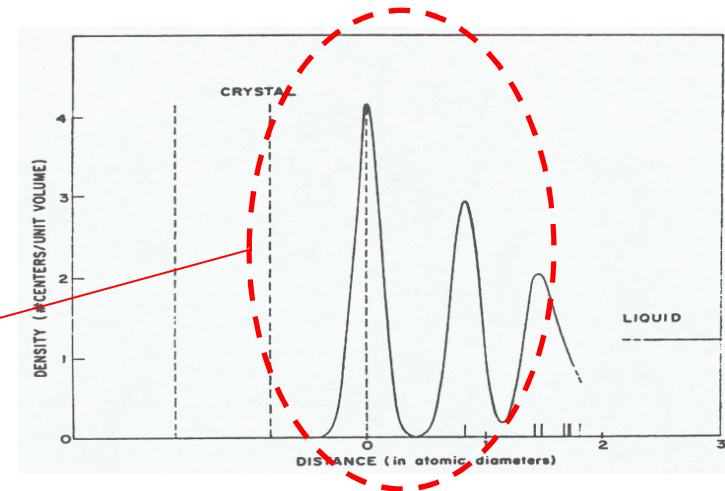
$$-T_f \cdot \Delta S_f$$

仮に固相中のEとSの
変化がない場合

2体間結合エネルギー

距離

常時この微細構造は
存在せず、揺らいでいる



固相

液相

界面層

$$G^{Solid} = G^{Liquid}$$

$$\Delta G_f$$

$$\Delta H_f$$

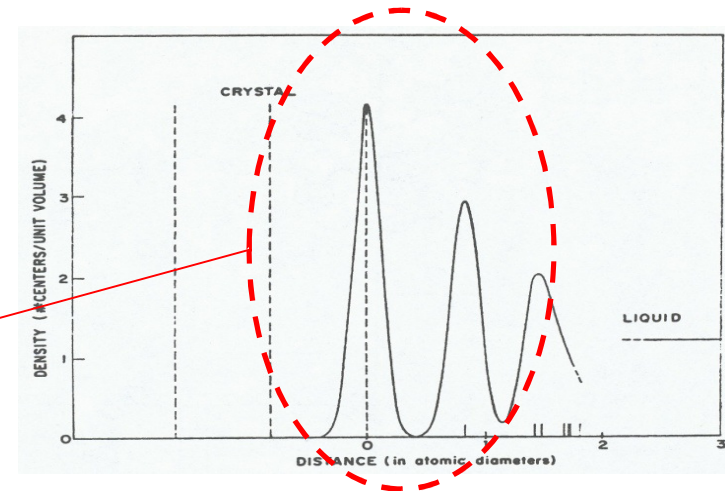
$$-T_f \cdot \Delta S_f$$

仮に固相中のEとSの
変化がなく、さらに
液相中のEの変化もない
場合

2体間結合エネルギー

距離

常時この微細構造は
存在せず、揺らいでいる



固相

液相

界面層

$$G^{Solid} = G^{Liquid}$$

$$\Delta G_f$$

動的平衡状態において、
界面を行き来する原子は
 $\delta G (= \delta H \text{ or } T\delta S)$ の自由エネルギーの
山を超える必要がある。

$$\Delta H_f$$

$$\delta H = \sum_i \delta H_i \propto \Delta H_f > 0$$

この斜線部の面積の和

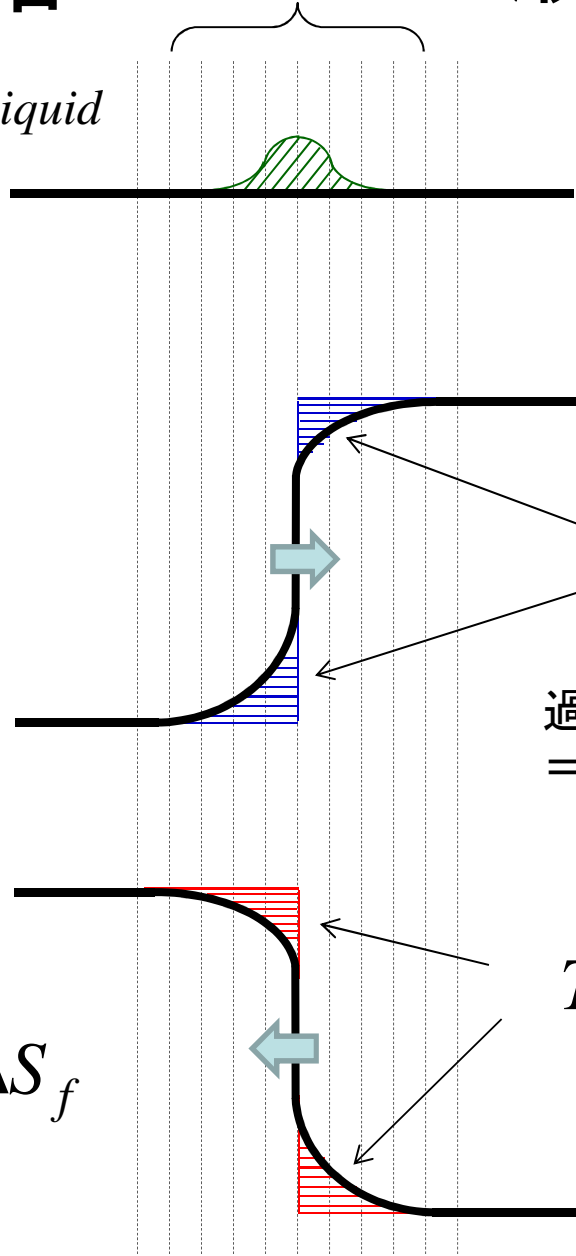
過剰な界面における自由エネルギーへの寄与
 $= \delta H \times P$
右向きへ移動する原子の割合

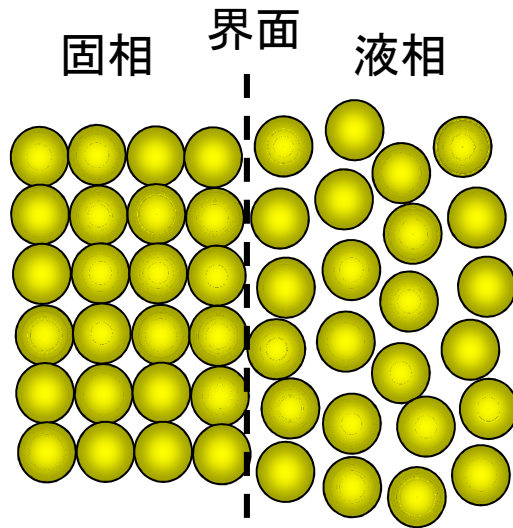
$$-T_f \cdot \Delta S_f$$

$$T\delta S = T(\sum_i \delta S_i) \propto T \cdot \Delta S_f > 0$$

この斜線部の面積の和

過剰な界面における自由エネルギーへの寄与
 $= T\delta H \times P$
左向きへ移動する原子の割合

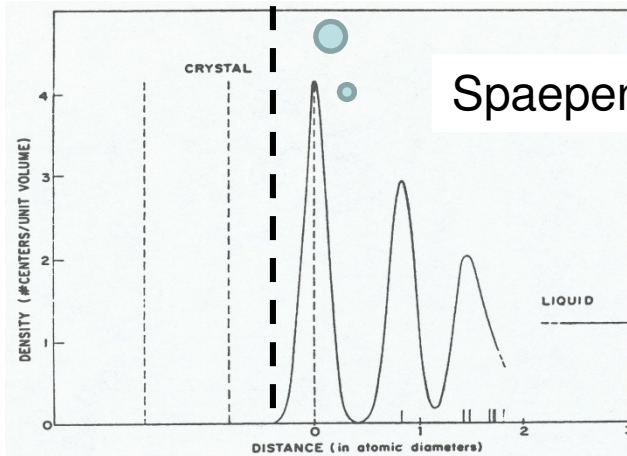




固液界面の液相中では、固相の原子配列の影響を受けて、液体中に規則的な原子配列が存在する可能性あり。

無秩序状態に対する大きなエントロピーから規則化の小さなエントロピーへ差が生じる。

無秩序が安定なのに、むりやり秩序づけられる
居心地の悪い状態



Spaepen et al.

$$\sigma^{Interface} = \frac{1}{A} \cdot \left(\frac{1}{4} \Delta H^{Melting} + \alpha \right)$$

融点 T_m において

$$\star G^{Liquid} = H^{Liquid} - T_m \cdot S^{Liquid}$$

$$= H^{Solid} - T_m \cdot S^{Solid} = G^{Solid}$$

$$\star H^{Liquid} - H^{Solid} = T_m \cdot (S^{Liquid} - S^{Solid})$$

$$\star \Delta H^{Melting} = T_m \cdot \Delta S^{Melting}$$

$\sigma^{Interface}$

$$= \frac{1}{A} \cdot \left(\frac{1}{4} \Delta H^{Melting} + \frac{1}{4} T_m \cdot \Delta S^{Melting} \right)$$

$$\begin{aligned}\sigma^{Interface} &= \frac{1}{A} \cdot (a \cdot \Delta H^{Melting} + b \cdot T_m \cdot \Delta S^{Melting}) \\ &= \frac{1}{A} \cdot \frac{\alpha}{2} (\Delta H^{Melting} + \beta \cdot T_m \cdot \Delta S^{Melting})\end{aligned}$$

もしも、 $\alpha=0.5$ 、 $\beta=1$ なら、最初のTurnbullの式に帰着

$$\begin{aligned}\sigma^{Interface} &= \frac{1}{A} \cdot \frac{0.5}{2} (\Delta H^{Melting} + 1 \cdot T_m \cdot \Delta S^{Melting}) \\ &= \frac{1}{A} \cdot \frac{1}{4} (\Delta H^{Melting} + T_m \cdot \Delta S^{Melting}) \\ &= \frac{1}{A} \cdot \frac{1}{2} (\Delta H^{Melting})\end{aligned}$$

合金の固液界面エネルギー：

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \{ (x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B}) + T \cdot (x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B}) \cdot \beta + H^{Ex}$$

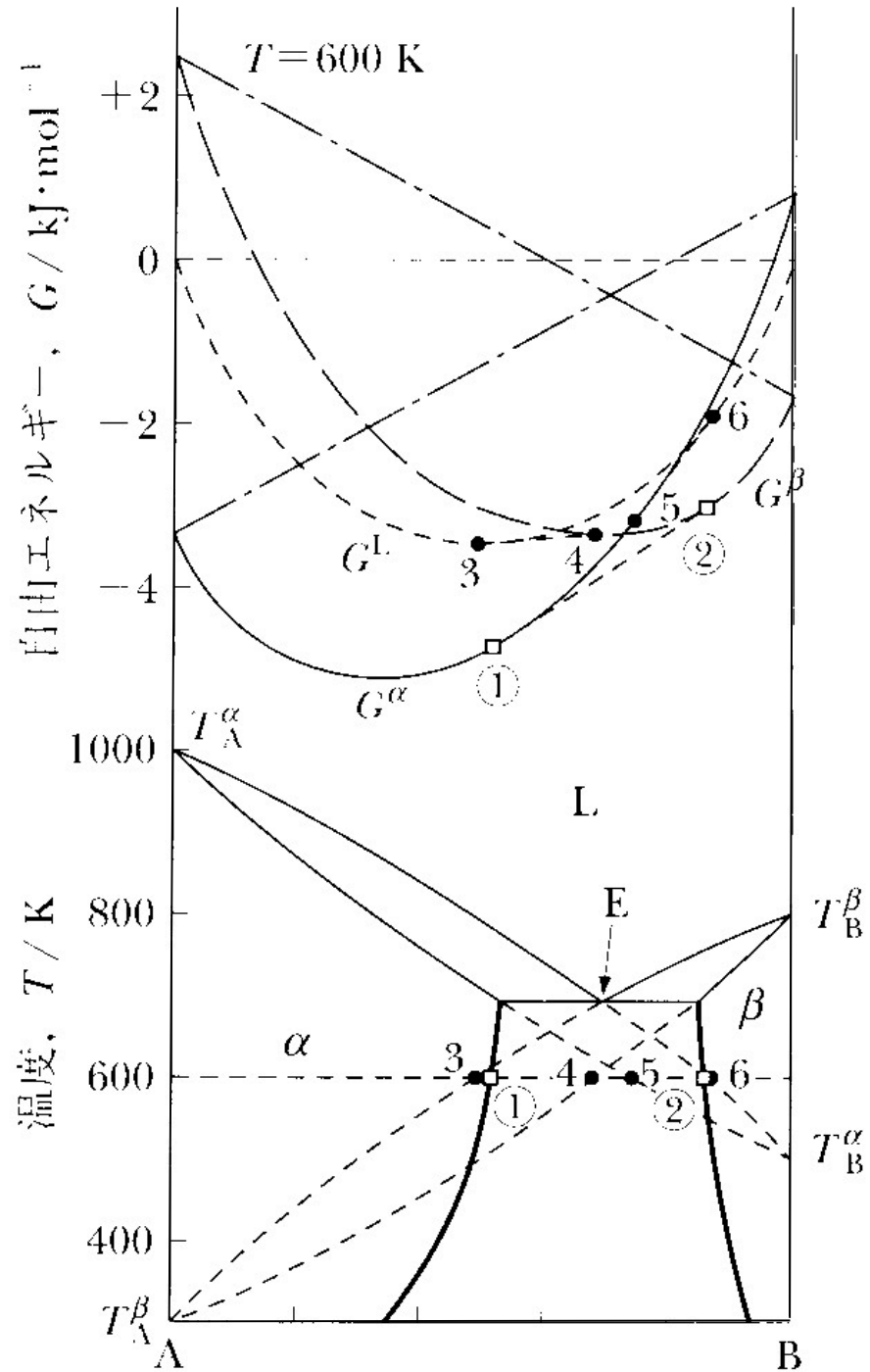
- (1) 純粋金属の固液間界面エネルギーは融解熱とエントロピーの寄与からなる。
- (2) 純金属の固液間界面エネルギーの温度依存性はプラス。
- (3) エントロピーの寄与は、純粋成分の融解のエントロピーに寄与率を掛けた値で評価。
- (4) 融解熱と融解のエントロピーの寄与は合金では、液相中の各成分のモル分率による加成性で表すことができると仮定する。
- (5) 結晶構造の違いによる固液界面の結合数を考慮して、面方位依存性を考慮する。

合金の固液界面エネルギー：

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \{ (x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B}) + T \cdot (x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B}) \cdot \beta + H^{Ex}$$

- (6) 固相の結晶構造を考慮するが、その固相の主たる成分を溶媒とした場合、溶質については、**溶媒と同じ結晶構造を取ると仮定**した場合の固液間界面エネルギーを考慮する。
- (7) **組成の異なる固相と液相が対峙**した際に新たに生じる**異種原子間相互作用**を考慮。
- (8) **混合のエントロピーの寄与**は、3次元と2次元平面では同じであると考え、界面を含む系では過剰量としては**存在しない**と仮定する。

共晶系において
2つの固相の
結晶構造が異なる場合



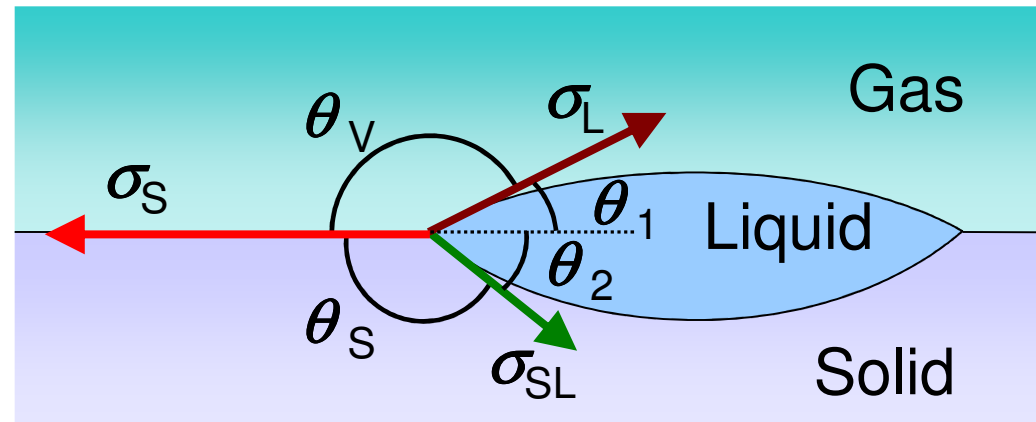
西澤泰二:「マイクロ組織
の熱力学」、講座・現代
の金属学 材料編2、
日本金属学会

実験原理

福田 敦

3種の界面エネルギー

- 液体の表面張力 σ_L
- 固体の表面エネルギー σ_S
- 固液界面エネルギー σ_{SL}



の水平・垂直方向のつりあい

$$\longrightarrow \frac{\sigma_{SL}}{\sin(180 - \theta_1)} = \frac{\sigma_L}{\sin(180 - \theta_2)} = \frac{\sigma_S}{\sin(\theta_1 + \theta_2)} \quad (\text{Dupreの式})$$

液滴の自発的な基板の溶解による θ_1, θ_2 の値
固気液三相界面の平衡形状の観察

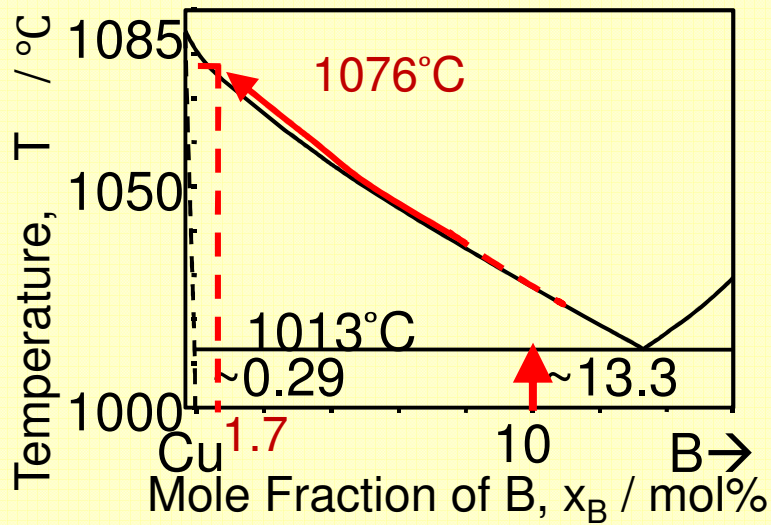
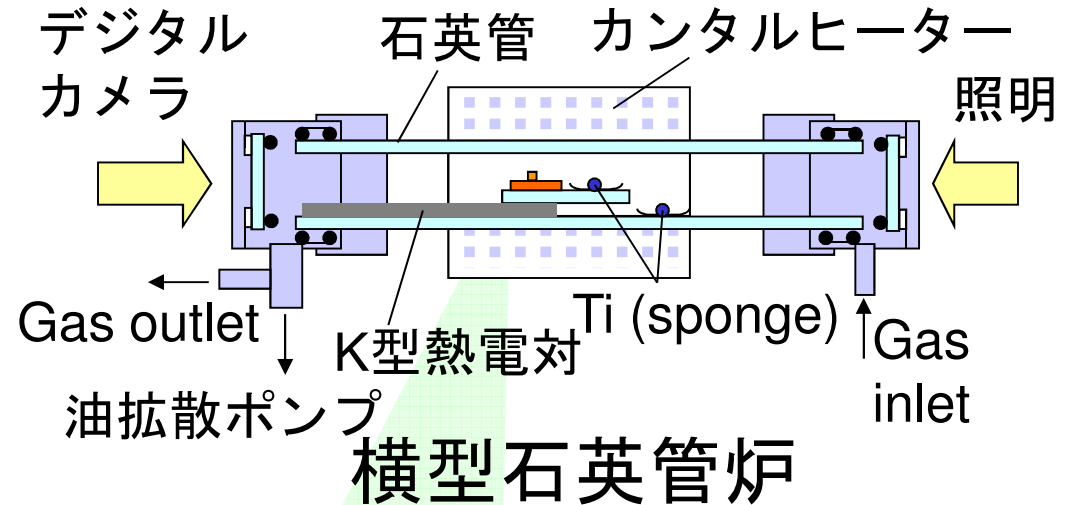
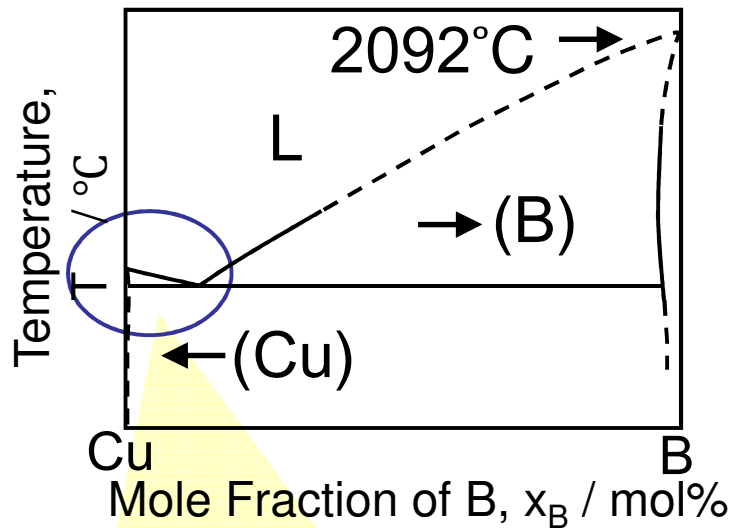
Butlerの式 \longrightarrow 合金液体の表面張力 σ_L

これらの値をDupreの式に代入することで、
固液界面エネルギー σ_{SL} と固体の表面エネルギー σ_S を評価する。

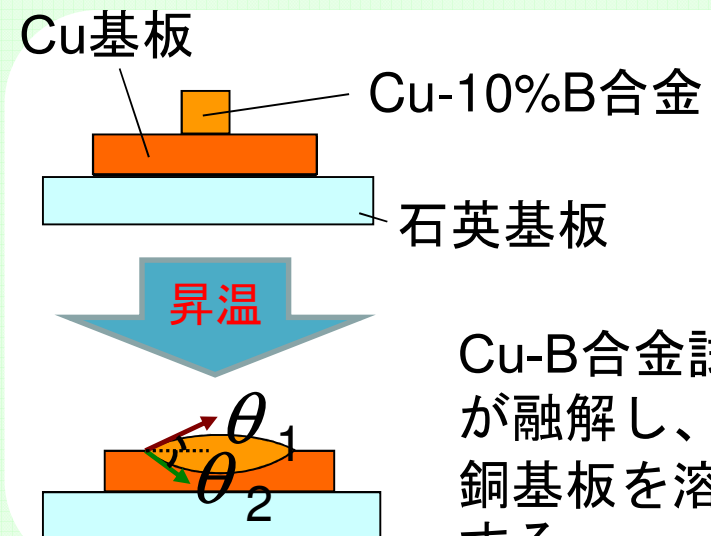
実験方法

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Cu-B系平衡状態図



Cuの融点近傍領域

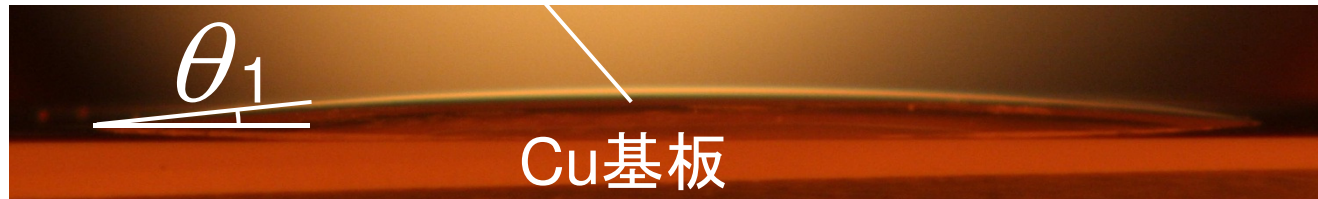
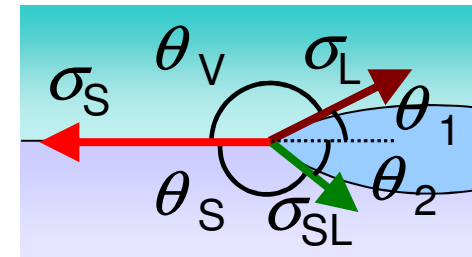


Cu-B合金試料が融解し、銅基板を溶解する。

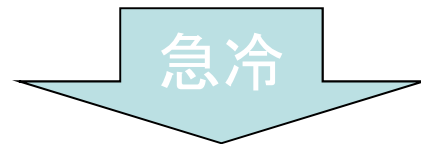
実験結果

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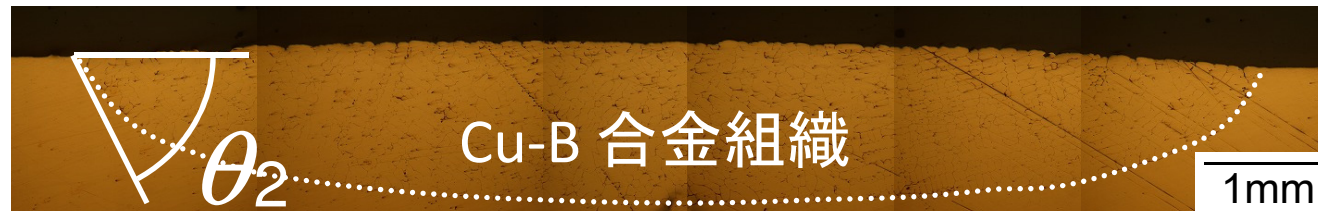
1076°C, Ar-10%H₂ 雰囲気下で5分間
保持された銅基板上のCu-B合金液滴



$\theta_1 = 6.4 \pm 0.4^\circ$



実験後の断面



$\theta_2 = 63.5 \pm 2.5^\circ$

Butlerの式より推算

σ_L (Cu-1.7at.%B, 1076°C) = 1366 mN/m

Dupreの式 $\left[\frac{\sigma_{SL}}{\sin(180 - \theta_1)} = \frac{\sigma_L}{\sin(180 - \theta_2)} = \frac{\sigma_S}{\sin(\theta_1 + \theta_2)} \right]$ に代入

固液界面エネルギー

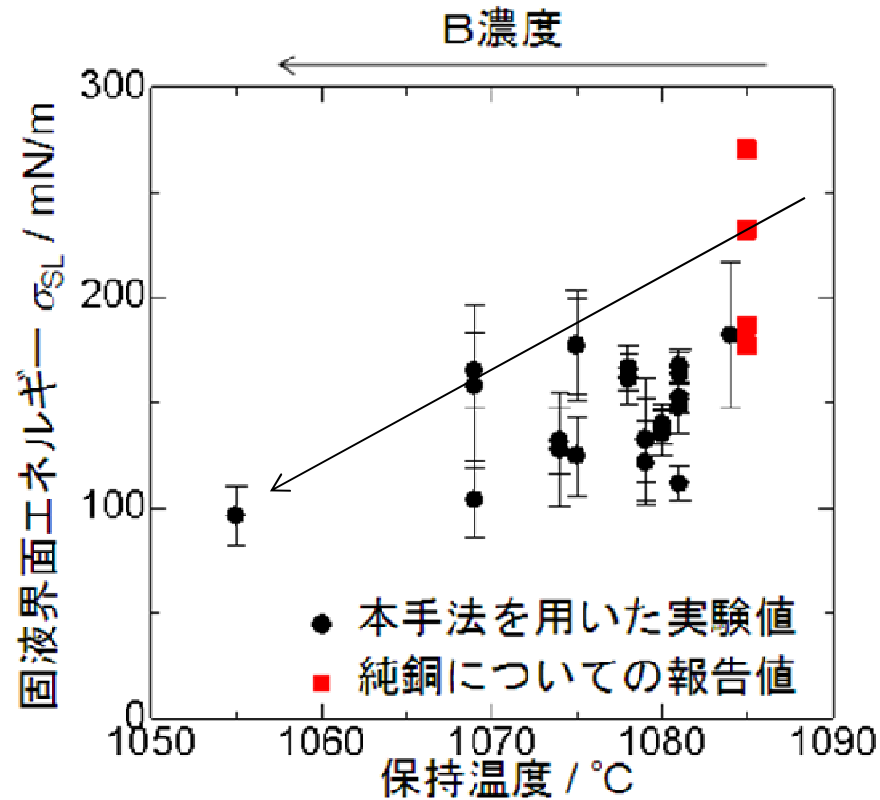
固体の表面エネルギー

$\sigma_{SL} = 170 \pm 16$ mN/m, $\sigma_S = 1435 \pm 60$ mN/m

cf. $\sigma_{SL} = 177 - 232$ mN/m (融点での純Cuの固液界面エネルギーの報告値)
 $\sigma_S = 1473$ mN/m (融点での純Cuの固体の表面エネルギーの報告値)

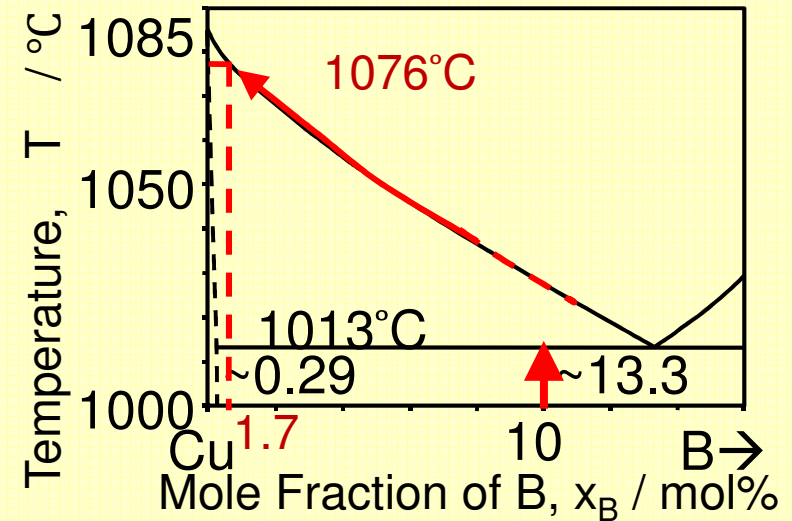
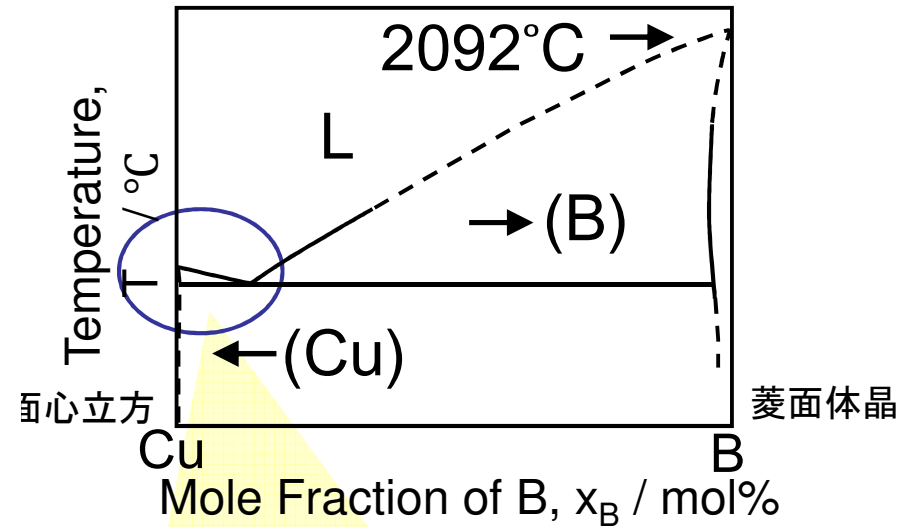
保持温度と実験結果

福田 敦

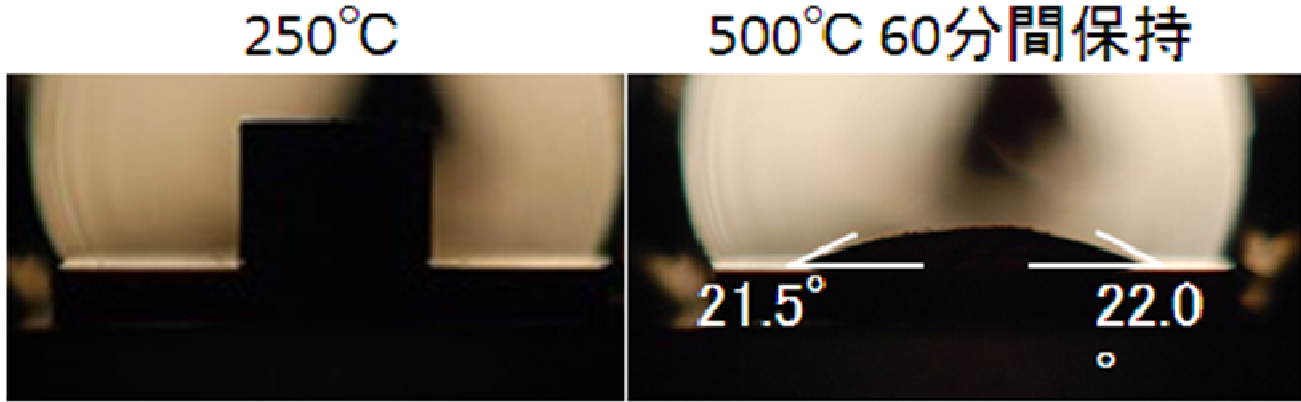


固液界面エネルギー σ_{SL}

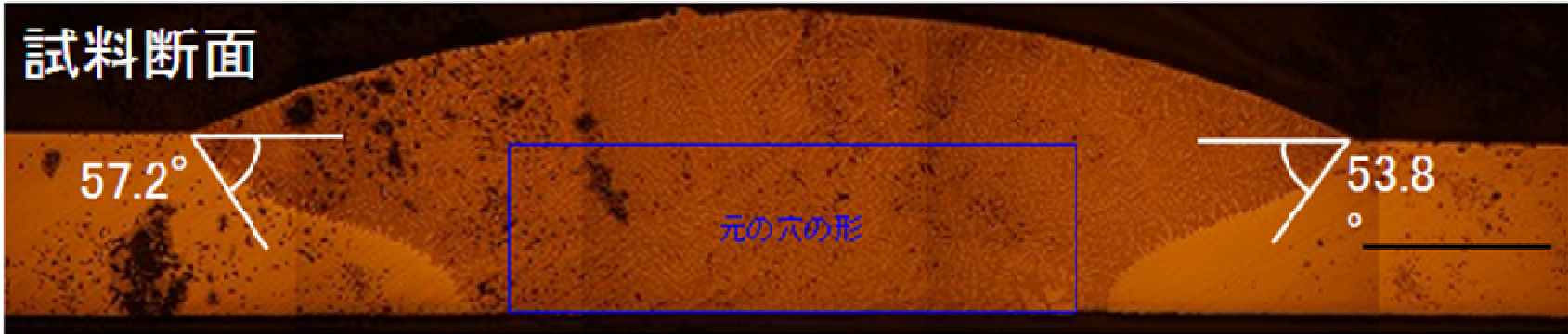
Cu-B系平衡状態図



Cuの融点近傍領域

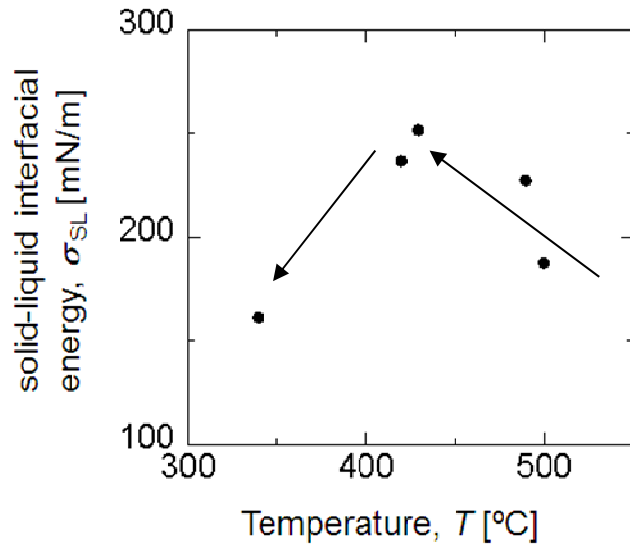


Ag-Bi合金におけるAg基板上の液滴形状の観察結果の一例

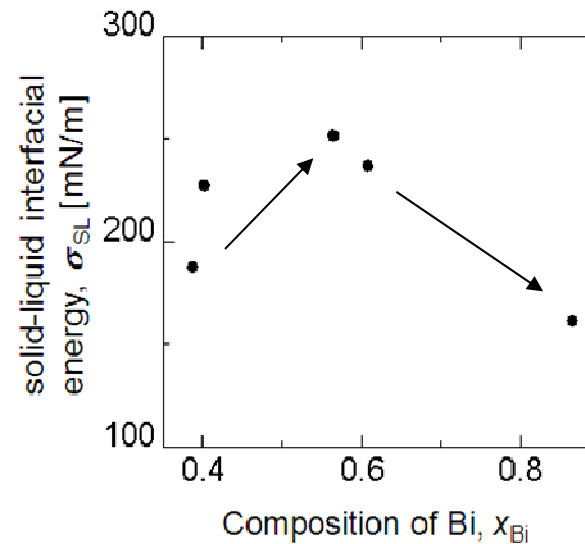


Ag-Bi合金における凝固試料の断面の観察結果の一例

$$\sigma^{LS} = \frac{1}{A} \cdot \frac{\alpha}{2} \cdot \{ (x_A^L \cdot \Delta H_{m,A} + x_B^L \cdot \Delta H_{m,B}) + T \cdot (x_A^L \cdot \Delta S_{m,A} + x_B^L \cdot \Delta S_{m,B}) \cdot \beta + H^{Ex}$$



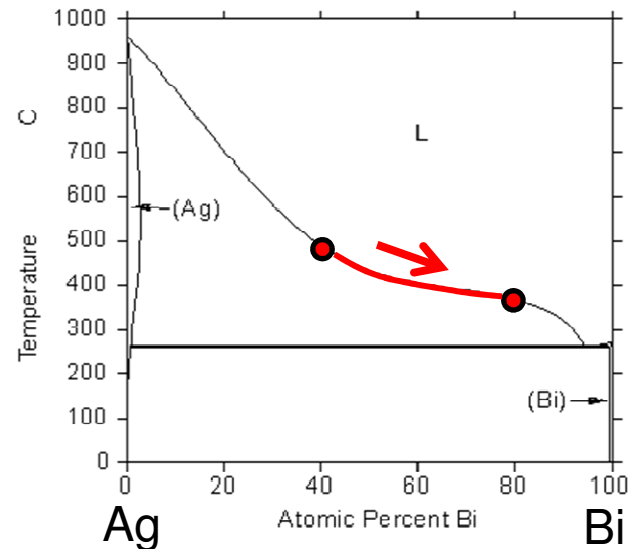
Ag-Bi系の固液界面エネルギーの温度依存性の測定結果

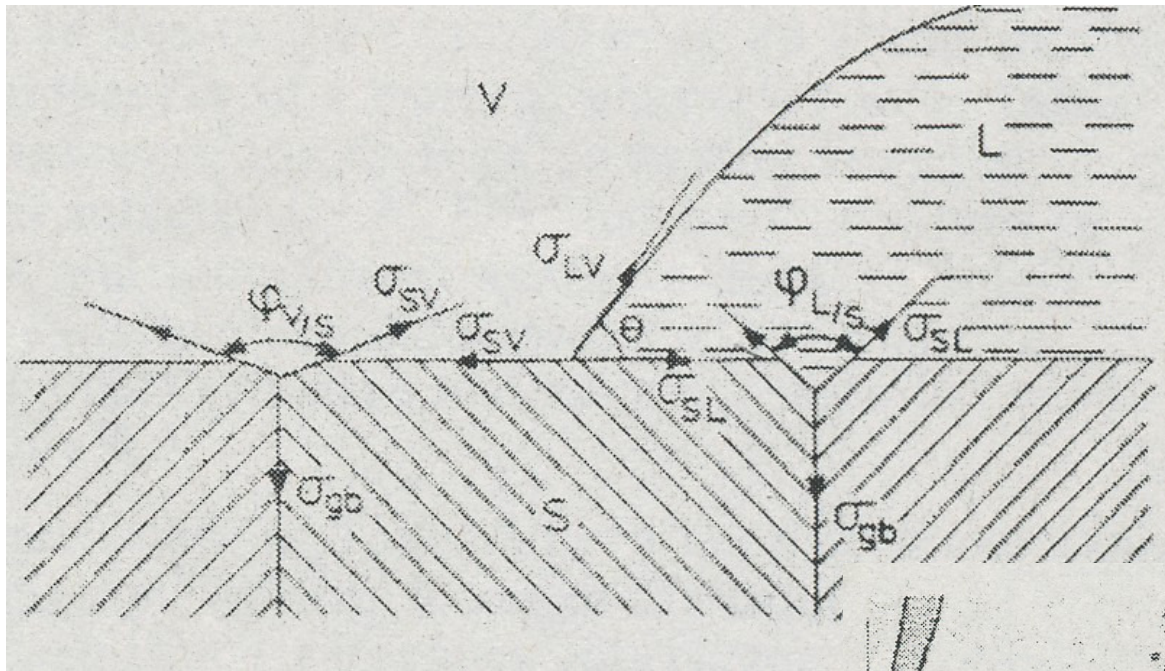


福田 敦

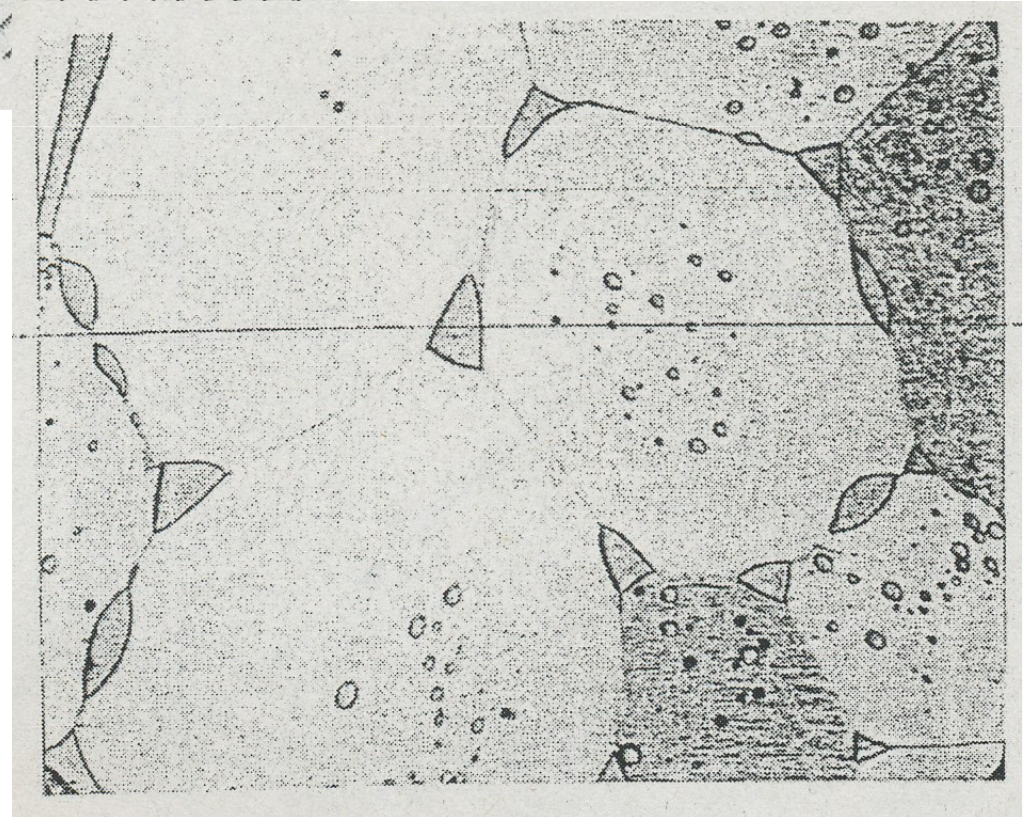
Ag-Bi系の固液界面エネルギーの組成依存性の測定結果

Ag-Bi2元系合金の状態図





2面角法



N.Eustathopoulos :Inter. Metals Review,
Vol.28 (1983), pp.189-210から引用

1. 合金の固液界面エネルギーは主として温度依存性に従って、組成とともに減少する。
2. 溶質成分が極端に高融点であるなど大きな融解熱、融解のエントロピーを持つ場合には、組成とともに、界面エネルギーは増加する。
3. プラスの相互作用が強い系では、界面エネルギー増加する。
4. 静滴法の実験は、多結晶の2面角測定法(数多くの結晶粒界の測定の統計的平均から界面エネルギーを決定)の一部に相当するのかも？