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Chemical potential energies of Sn-eutectic formations versus Sn-intermetallic formations

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Eutectic alloys play a significant role on reactive wetting in solder/braze applications. Good solders are low melting temperature alloys that are eutectics or other two-phase mixtures that are close to eutectic compositions. They bond to the substrate by reacting chemically to form intermetallic compounds. The driving force for reactive wetting is estimated, by Yost and Romig [1] in 1988, to be $1/2\pi r(dE/dr) = \sigma + \Gamma(\theta)$, where σ is the driving force of chemical potential energy for compound formation and $\Gamma(\theta)$ corresponds to the driving force of imbalance in interfacial tensions. They estimated that the driving force for intermetallic compound formation is much greater than imbalance of interfacial tensions when the thickness of compound is taken to be 1 μm. The purpose of this study is to investigate and compare chemical potential energies for one mole of molten Sn-X eutectic, as seen in Fig. 1, at the eutectic temperature and Sn-intermetallic formations at the melting point of Sn, since Sn is the main component for the associated solder alloys. This study is focused on effective energies of eutectic compounds to react with solid metal substrate for wetting at the eutectic temperatures. Also, at above the eutectic temperature and depending on formation energies, intermetallic compounds should occur either between Sn or X and solid substrate metal, M. Sn-substrate metal (M) interactions are the only ones considered in this study.

The understanding of intermetallic phase formation is important because of the significant contribution that the various intermetallics make to the stability of the solder connection. Sn-eutectic alloys have many advantages in solder applications, because the main constituent of these alloys, tin, is very ductile; any stresses that may develop can easily be relieved through plastic deformation of the joints. Likewise, by using Sn-eutectic alloys, soldering can be carried out at the lowest possible temperature and the eutectic solder wets surfaces easily and quickly. In addition, eutectic alloys produce smooth and shiny solder joints. Though the eutectic alloys have many such advantages, there is always an attempt to use a lower tin content solder to reduce cost, since the price of solder is directly related to the tin content.

To investigate chemical potential energies of Sn-eutectic alloys, consider one unit of molten Sn-X eutectic, that has one mole of Sn, on a clean and pure metal (M) substrate. At above the eutectic temperature molten solder comes into contact and reacts with the solid substrate metal, M, through chemical potential and surface energy differences. At this point, active constituent of Sn-X eutectic solder reacts with the substrate metal M and substrate metal M dissolves into the molten Sn-X eutectic. Both processes will form intermetallic compounds in the interfacial region between the molten solder and the base metal. We focused on Sn-M reactions to investigate the energies of Sn-intermetallic compounds, in the form of SnM_x, because these intermetallic compounds should play an important role in strengthening the soldered joint, its strength of bond to substrate and achievement of high joint strength.

The shape of a drop of molten eutectic alloy on a solid substrate is determined by the interaction of forces such as solid-liquid interfacial energy (γ_{sl}), solid-vapor interfacial energy (γ_{sv}), and liquid-vapor surface energy (γ_{lv}). The Young-Dupree Equation, as illustrated in Fig. 2, characterizes this balance of interfacial tensions at equilibrium,

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv}\mathrm{Cos}\theta$$

To investigate chemical potential energies for a eutectic phase, chemical potential energies of eutectic

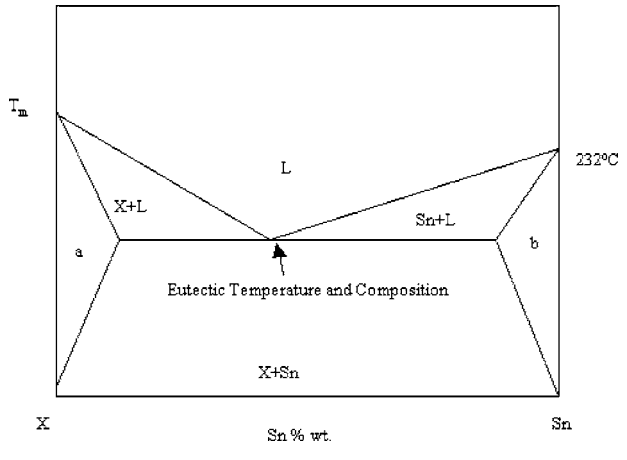

Figure 1 Sn-X eutectic diagram.

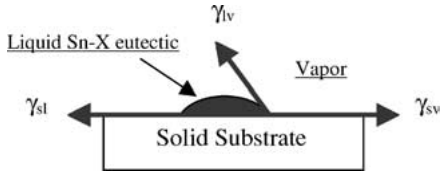

Figure 2 Sessile-drop of molten Sn-eutectic on substrate metal.

components for Sn and X are calculated by

$$\Delta\bar{G}_{Sn} = \mu_{Sn}\, dn_{Sn} \quad (1)$$

$$\Delta\bar{G}_{x} = \mu_{X}\, dn_{X} \quad (2)$$

The energy of formation of a eutectic phase (Sn-X) is calculated by

$$\Delta G = X_{Sn}\Delta\bar{G}_{Sn} + X_{x}\Delta\bar{G}_{x} \quad (3)$$

The thickness of Sn-eutectic compound on the substrate metal M as well as the thickness of Sn-intermetallic compound are assumed to be 1 μm as in [1]. The chemical potential energies and surface energies of Sn-eutectic binaries are in Table I. Likewise, molten Sn-eutectics, considered on the transition metal substrates, and their chemical potential energies are in Tables II–VII.

The investigation of chemical potential energies for Sn-intermetallic phase, at the melting point of Sn, where two metals react during the spreading, one mole of Sn and M is transferred into the compound forming an intermetallic compound, SnM_x,

$$Sn + xM \rightarrow SnM_x \quad (4)$$

The free energy of formation of this phase is calculated by

$$\Delta G = X_{Sn}\Delta\bar{G}_{Sn} + X_{X}\Delta\bar{G}_{X}$$

By the estimation of Yost and Romig [1], σ is the driving force of reactive wetting being the chemical potential energy of intermetallic compound formation and is expressed as

$$\sigma = (\rho_M l_M / xM_M)\Delta G \quad (5)$$

where

ρ_m: density of substrate metal
l_m: assumed thickness in μm
M_m: atomic weight of substrate metal
x: amount of substrate metal reacting with one mole of Sn.
ΔG: formation energies of the intermetallic compounds.

Chemical potential energies of Sn-intermetallics, with only molten Sn reacting, are tabulated for the same substrate metals in Table VIII. The significance of these energies, compared to those of Sn-eutectic alloys reacting at the eutectic temperatures, are shown in Tables II–VIII.

TABLE I Formation energies for X-Sn eutectic alloys at the eutectic temperatures

Binary	Eutectic comp.%	T_E (K)	ΔG (T) kJ/mol [2, 3]	ΔG (T) kJ/mol for 1 mole of Sn	γ N/mx10^3 [4]
Al-Sn	3Al + 97Sn	502	−26.970	−33.012	
Bi-Sn	42Bi + 58Sn	411.5	−22.602	−46.315	461
Cd-Sn	32Cd + 68Sn	450	−24.116	−42.088	590
In-Sn	51In + 49Sn	393	−23.117	−56.108	175
Pb-Sn	37Pb + 63Sn	456	−26.706	−50.388	477
Zn-Sn	9Zn + 91Sn	471	−24.953	−32.156	580

TABLE II Chemical potential energies of Sn-intermetallics formed by reaction of Al-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / xM_M \times 10^{-5}$	σ kJ/m$^2\times10^6$
Al-Sn Eutectic	For one mole of Sn at eutectic temp. −33.012	Ti	Ti_2Sn	0.47	−1.55
		V	V_2Sn_3	1.75	−5.77
		Mn	$MnSn_2$	2.7	−8.91
		Fe	FeSn	1.4	−4.62
		Co	CoSn	1.5	−4.95
		Ni	NiSn	1.51	−4.98
		Cu	Cu_3Sn	0.46	−1.52
		Y	YSn_3	1.5	−4.95
		Zr	$ZrSn_2$	1.4	−4.62
		Nb	$NbSn_2$	1.84	−6.07
		Mo	$MoSn_2$	2.1	−6.93
		Ru	Ru_2Sn_3	1.82	−6.00
		Rh	$RhSn_4$	4.8	−15.84
		Pd	$PdSn_4$	4.5	−14.85
		Ag	Ag_3Sn	3.24	−10.69
		Hf	$HfSn_2$	1.49	−4.91
		Ta	Ta_2Sn_3	1.37	−4.52
		Pt	$PtSn_4$	4.39	−14.50
		Au	AuSn	0.98	−3.23

TABLE III Chemical potential energies of Sn-intermetallics formed by reaction of Bi-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / x M_M \times 10^{-5}$	σ kJ/m$^2 \times 10^6$
Bi-Sn Eutectic	For one mole of Sn at eutectic temp. −46.315	Ti	Ti_2Sn	0.47	−2.17
		V	V_2Sn_3	1.75	−8.11
		Mn	$MnSn_2$	2.7	−12.53
		Fe	FeSn	1.4	−6.48
		Co	CoSn	1.5	−6.94
		Ni	NiSn	1.51	−6.99
		Cu	Cu_3Sn	0.46	−2.13
		Y	YSn_3	1.5	−6.94
		Zr	$ZrSn_2$	1.4	−6.48
		Nb	$NbSn_2$	1.84	−8.52
		Mo	$MoSn_2$	2.1	−9.72
		Ru	Ru_2Sn_3	1.82	−8.42
		Rh	$RhSn_4$	4.8	−22.22
		Pd	$PdSn_4$	4.5	−20.83
		Ag	Ag_3Sn	3.24	−15.00
		Hf	$HfSn_2$	1.49	−6.90
		Ta	Ta_2Sn_3	1.37	−6.34
		Pt	$PtSn_4$	4.39	−20.32
		Au	AuSn	0.98	−4.53

TABLE IV Chemical potential energies of Sn-intermetallics formed by reaction of Cd-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / x M_M \times 10^{-5}$	σ kJ/m$^2 \times 10^6$
Cd-Sn Eutectic	For one mole of Sn at eutectic temp. −42.088	Ti	Ti_2Sn	0.47	−1.97
		V	V_2Sn_3	1.75	−7.35
		Mn	$MnSn_2$	2.7	−11.34
		Fe	FeSn	1.4	−5.88
		Co	CoSn	1.5	−6.3
		Ni	NiSn	1.51	−6.34
		Cu	Cu_3Sn	0.46	−1.93
		Y	YSn_3	1.5	−6.3
		Zr	$ZrSn_2$	1.4	−5.88
		Nb	$NbSn_2$	1.84	−7.72
		Mo	$MoSn_2$	2.1	−8.82
		Ru	Ru_2Sn_3	1.82	−7.64
		Rh	$RhSn_4$	4.8	−20.16
		Pd	$PdSn_4$	4.5	−18.9
		Ag	Ag_3Sn	3.24	−13.6
		Hf	$HfSn_2$	1.49	−6.26
		Ta	Ta_2Sn_3	1.37	−5.75
		Pt	$PtSn_4$	4.39	−18.43
		Au	AuSn	0.98	−4.11

TABLE V Chemical potential energies of Sn-intermetallics formed by reaction of In-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / x M_M \times 10^{-5}$	σ kJ/m$^2 \times 10^6$
In-Sn Eutectic	For one mole of Sn at eutectic temp. −56.108	Ti	Ti_2Sn	0.47	−2.63
		V	V_2Sn_3	1.75	−9.81
		Mn	$MnSn_2$	2.7	−15.12
		Fe	FeSn	1.4	−7.84
		Co	CoSn	1.5	−8.41
		Ni	NiSn	1.51	−8.45
		Cu	Cu_3Sn	0.46	−2.57
		Y	YSn_3	1.5	−8.41
		Zr	$ZrSn_2$	1.4	−7.84
		Nb	$NbSn_2$	1.84	−10.32
		Mo	$MoSn_2$	2.1	−11.76
		Ru	Ru_2Sn_3	1.82	−10.21
		Rh	$RhSn_4$	4.8	−26.88
		Pd	$PdSn_4$	4.5	−25.24
		Ag	Ag_3Sn	3.24	−18.14
		Hf	$HfSn_2$	1.49	−8.34
		Ta	Ta_2Sn_3	1.37	−7.67
		Pt	$PtSn_4$	4.39	−24.58
		Au	AuSn	0.98	−5.48

TABLE VI Chemical potential energies of Sn-intermetallics formed by reaction of Pb-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / x M_M \times 10^{-5}$	σ kJ/m$^2 \times 10^6$
Pb-Sn Eutectic	For one mole of Sn at eutectic temp. −50.388	Ti	Ti_2Sn	0.47	−2.35
		V	V_2Sn_3	1.75	−8.75
		Mn	$MnSn_2$	2.7	−13.58
		Fe	FeSn	1.4	−7.04
		Co	CoSn	1.5	−7.54
		Ni	NiSn	1.51	−7.55
		Cu	Cu_3Sn	0.46	−2.31
		Y	YSn_3	1.5	−7.54
		Zr	$ZrSn_2$	1.4	−7.04
		Nb	$NbSn_2$	1.84	−9.25
		Mo	$MoSn_2$	2.1	−10.56
		Ru	Ru_2Sn_3	1.82	−9.15
		Rh	$RhSn_4$	4.8	−24.14
		Pd	$PdSn_4$	4.5	−22.63
		Ag	Ag_3Sn	3.24	−16.29
		Hf	$HfSn_2$	1.49	−7.45
		Ta	Ta_2Sn_3	1.37	−6.85
		Pt	$PtSn_4$	4.39	−21.95
		Au	AuSn	0.98	−4.93

TABLE VII Chemical potential energies of Sn-intermetallics formed by reaction of Zn-Sn eutectic with substrate M

Eutectic	ΔG (kJ/mol)	Substrate metal (M)	Form	$\rho_M l_M / x M_M \times 10^{-5}$	σ kJ/m$^2 \times 10^6$
Zn-Sn Eutectic	For one mole of Sn at eutectic temp. −32.156	Ti	Ti_2Sn	0.47	−1.50
		V	V_2Sn_3	1.75	−5.61
		Mn	$MnSn_2$	2.7	−8.66
		Fe	FeSn	1.4	−4.49
		Co	CoSn	1.5	−4.81
		Ni	NiSn	1.51	−4.84
		Cu	Cu_3Sn	0.46	−1.47
		Y	YSn_3	1.5	−4.81
		Zr	$ZrSn_2$	1.4	−4.49
		Nb	$NbSn_2$	1.84	−5.90
		Mo	$MoSn_2$	2.1	−6.74
		Ru	Ru_2Sn_3	1.82	−5.84
		Rh	$RhSn_4$	4.8	−15.4
		Pd	$PdSn_4$	4.5	−14.44
		Ag	Ag_3Sn	3.24	−10.40
		Hf	$HfSn_2$	1.49	−4.78
		Ta	Ta_2Sn_3	1.37	−4.40
		Pt	$PtSn_4$	4.39	−14.09
		Au	AuSn	0.98	−3.14

TABLE VIII Surface tension of metal substrates M, formation energies and chemical potential energies for M_xSn compounds at melting point of Sn (505 K)

M	γN/m $\times 10^3$ [5]	Form	Reaction kJ/mol	$\Delta G \times 10^{-5}$	$\rho_M l_M / x M_M \times 10^6$	σkJ/m^2
Ti	1880	Ti_2Sn	$Sn + 2Ti \rightarrow Ti_2Sn$	−20.530	0.47	−0.96
V	1950	V_2Sn_3	$Sn + 2/3V \rightarrow 1/3V_2Sn_3$	−7.655	1.75	−1.34
Mn	1150	$MnSn_2$	$Sn + 1/2Mn \rightarrow 1/2MnSn_2$	−12.155	2.7	−3.21
Fe	532	FeSn	$Sn + Fe \rightarrow FeSn$	−23.649	1.4	−3.31
Co	1870	CoSn	$Sn + Co \rightarrow CoSn$	−22.166	1.5	−3.31
Ni	2285	NiSn	$Sn + Ni \rightarrow NiSn$	−22.128	1.51	−3.34
Cu	820	Cu_3Sn	$Sn + 3Cu \rightarrow Cu_3Sn$	−20.560	0.46	−0.94
Y		YSn_3	$Sn + 1/3Y \rightarrow 1/3YSn_3$	−8.885	1.5	−1.33
Zr	1480	$ZrSn_2$	$Sn + 1/2Zr \rightarrow 1/2ZrSn_2$	−12.710	1.4	−1.78
Nb	2020	$NbSn_2$	$Sn + 1/2Nb \rightarrow 1/2NbSn_2$	−12.500	1.84	−2.30
Mo	2250	$MoSn_2$	$Sn + 1/2Mo \rightarrow 1/2MoSn_2$	−11.845	2.1	−2.48
Ru	2250	Ru_2Sn_3	$Sn + 2/3Ru \rightarrow 1/3Ru_2Sn_3$	−7.619	1.82	−1.38
Rh	2000	$RhSn_4$	$Sn + 1/4Rh \rightarrow 1/4RhSn_4$	−6.377	4.8	−3.06
Pd	1500	$PdSn_4$	$Sn + 1/4Pd \rightarrow 1/4PdSn_4$	−6.538	4.5	−2.94
Ag	1026	Ag_3Sn	$Sn + 3Ag \rightarrow Ag_3Sn$	−23.972	3.24	−7.76
Hf	1460	$HfSn_2$	$Sn + 1/2Hf \rightarrow 1/2HfSn_2$	−13.105	1.49	−1.95
Ta	2360	Ta_2Sn_3	$Sn + 2/3Ta \rightarrow 1/3Ta_2Sn_3$	−8.504	1.37	−1.16
Pt	1720	$PtSn_4$	$Sn + 1/4Pt \rightarrow 1/4PtSn_4$	−6.634	4.39	−2.91
Au	1130	AuSn	$Sn + Au \rightarrow AuSn$	−26.359	0.98	−2.58

Simple Sn-eutectic binary alloys and pure Sn are selected for investigation for their chemical potential energies of Sn-intermetallic formations. In both cases, same formations of Sn-intermetallic compounds are seen to occur. In the use of molten Sn-X eutectic alloys, Sn-intermetallic compounds are seen to occur with lower energies than in the use of molten Sn on the same substrates per mole of Sn. Melting point of active constituents of the eutectics, such as those of Al, Bi, Cd, Pb and Zn are higher than that of Sn. In contrast, melting point of In is lower than that of Sn, in Sn-In binary eutectic, and this shows the lowest eutectic temperature and highest eutectic formation energy. The active constituents of the eutectics are seen to play an important role in the resultant eutectic temperature in their inducing lower melting points than that of Sn.

On the other hand, substrate material properties, such as density and atomic weight are other important issues and, the values of the parameter ($\rho_{\mathrm{M}}\mathrm{l}_M/\mathrm{xM}_{\mathrm{M}}$) in the Table VIII, are seen to play a significant role on chemical potential energies of intermetallic compound formation. Among the investigated transition metals, Rh, Pd and Pt have the highest values for this parameter and they show the highest chemical potential energies. In contrast, Au, Ti and Cu have the lowest values for this parameter and they gave the lowest energy values, as seen in the table.

As the driving force for reactive wetting, chemical potential energy consists of formation energy and the aforementioned parameter value for the substrate, and is expressed as $\sigma = \Delta G(\rho_{\mathrm{M}}\mathrm{l}_{\mathrm{M}}/\mathrm{xM}_{\mathrm{M}})$. The parameter value for substrate is seen to be more effective (in Tables II–VIII) than formation energies (ΔG) on determining the chemical potential energies for Sn-intermetallics formation.

As can be seen in the computations made, chemical potential energies are more effective than surface energies in the formation of Sn-intermetallic compounds in both Sn-eutectic compounds and molten Sn on the substrate metal. Although eutectic temperatures are lower than the melting point of Sn, in the case of Sn-eutectic alloys used to form Sn-intermetallics, chemical potential energies exhibit higher values than for molten Sn on the substrate metal M. Furthermore, substrate parameter, $\rho_{\mathrm{M}}\mathrm{l}_{\mathrm{M}}/\mathrm{xM}_{\mathrm{M}}$, plays a significant role on determining the chemical potential energies of Sn-intermetallics formed with transition metals.

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