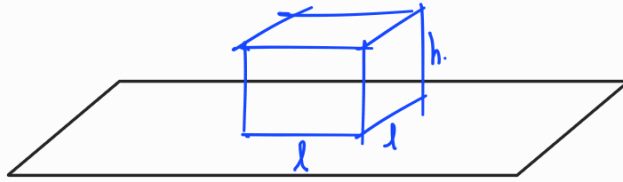


HW4 신소재공학과 20222571 최찬식

1.



Formation of nuclei : volume + surface + interface

volume : $l^2 h$, surface : $4lh + l^2$, interface : l^2 .

Energy change. $\Delta G = -l^2 h \Delta G_v + (4lh + l^2) \gamma_{cv} + l^2 \gamma_{cl} - l^2 \gamma_{vs}$.

Critical size where the value of $\frac{\partial \Delta G}{\partial l}$ (l is a size variable) becomes zero.

Since h and l are independent, partial differentiation of each is necessary to determine critical size.

for l ,

$$\begin{aligned} \frac{\partial \Delta G}{\partial l} &= -2lh \Delta G_v + (4h + 2l) \gamma_{cv} + 2l(\gamma_{cl} - \gamma_{vs}) \\ &= -2lh \Delta G_v + 4h \gamma_{cv} + 2l(\gamma_{cv} + \gamma_{cl} - \gamma_{vs}). \quad \gamma_{cv} + \gamma_{cl} - \gamma_{vs} = \Delta \gamma \\ &= -2lh \Delta G_v + 4h \gamma_{cv} + 2l \Delta \gamma. \end{aligned}$$

$$\begin{aligned} \frac{\partial \Delta G}{\partial l} \Big|_{h, l^*} &= -2l^* h^* \Delta G_v + 4h^* \gamma_{cv} + 2l^* \Delta \gamma = 0 \\ &= -8h^* \gamma_{cv} + 4h^* \gamma_{cv} + \frac{8h^* \gamma_{cl}}{\Delta G_v} \Delta \gamma \\ \Rightarrow -h^* + \frac{2\Delta \gamma}{\Delta G_v} &= 0. \quad \therefore h^* = \frac{2\Delta \gamma}{\Delta G_v} \end{aligned}$$

for h ,

$$\frac{\partial \Delta G}{\partial h} = -l^2 \Delta G_v + 4l \gamma_{cv}.$$

$$\frac{\partial \Delta G}{\partial h} \Big|_{h^*, l^*} = -l^{*2} \Delta G_v + 4l^* \gamma_{cv} = 0 \quad \underline{l^* = \frac{4\gamma_{cv}}{\Delta G_v}} \quad \dots (1).$$

Energy barrier of nucleation.

$$\begin{aligned} \Delta G &= -\left(\frac{4\gamma_{cv}}{\Delta G_v}\right)^2 \left(\frac{2\Delta \gamma}{\Delta G_v}\right) \Delta G_v + \frac{32\gamma_{cv} \Delta \gamma}{\Delta G_v^2} \gamma_{cv} + \frac{16\gamma_{cv}^2}{\Delta G_v^2} \Delta \gamma \\ &= \frac{\gamma_{cv}^2 \Delta \gamma}{\Delta G_v^2} (-32 + 32 + 16) \\ &= \frac{16\gamma_{cv}^2 \Delta \gamma}{\Delta G_v^2} \end{aligned}$$

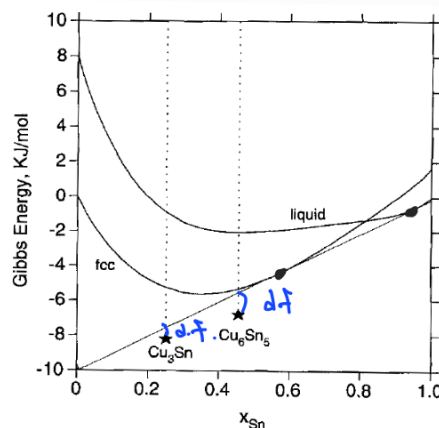
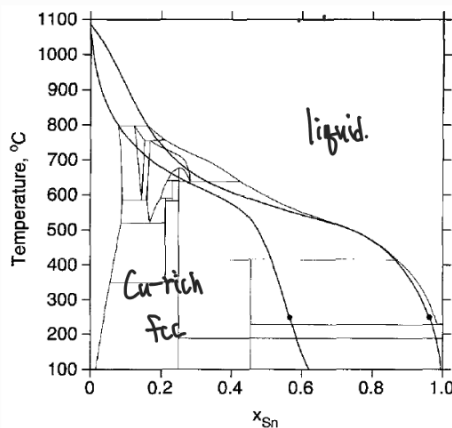
2.(1) "Prediction of interface reaction products between Cu and various solder alloys by thermodynamic calculation"

Introduction

To reduce Pb content on the solder alloy because of health and environmental reason, various Sn-based alloys have been suggested. The reaction products between substrates and solder alloys should be known for better mechanical properties of the interface. Among the various intermetallic compounds, firstly formed one is deterministic for the substrate/solder alloy joint. By thermodynamic simulation, it can be concluded that the one with highest driving force would be initially formed.

Basic assumptions — Cu-Sn system.

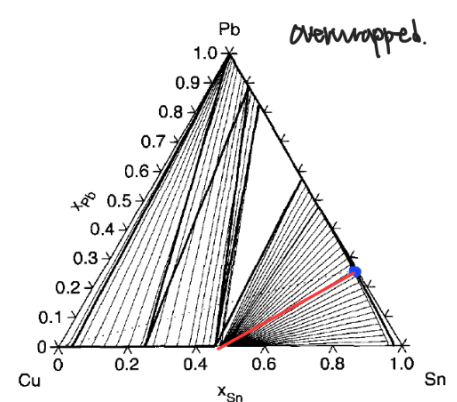
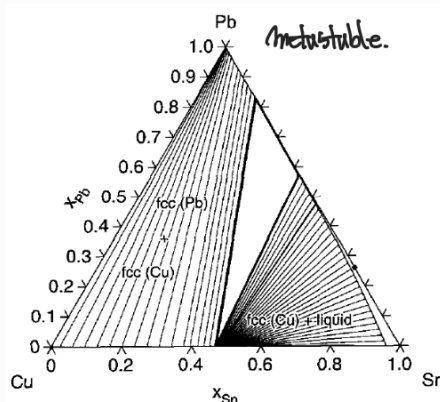
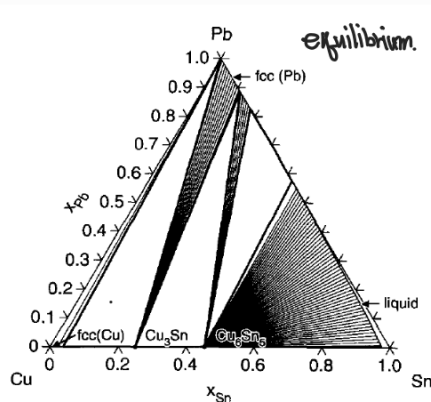
Diffusion controlled reaction, local equilibrium are assumed. The metastable equilibrium can be calculated as thick lines. The phase boundary has narrower area. By drawing common tangent line at given temperature, the driving force of each intermetallic compound formation can be estimated. Cu_6Sn_5 has the highest driving force.



d.f: free energy discrepancy (vertical distance) of a compound and a metastable common tangent line.

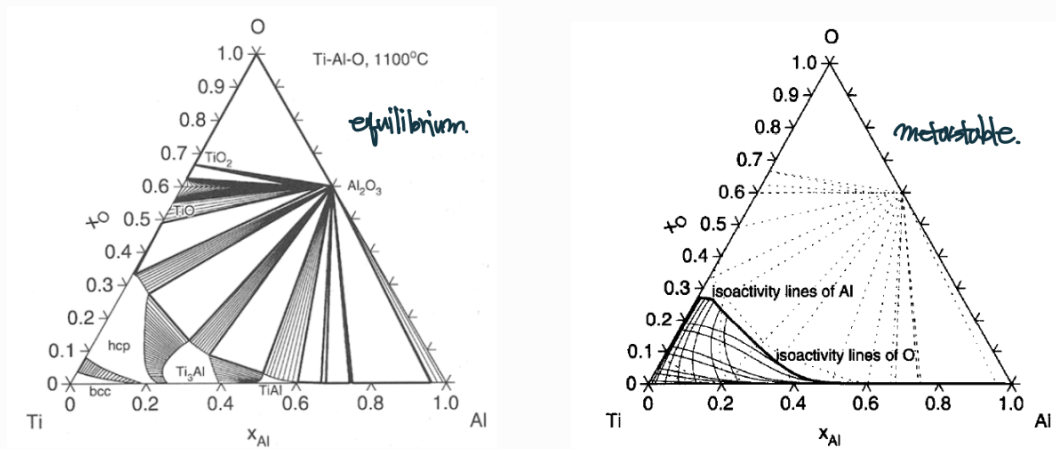
Cu-Sn-Pb system.

The above method can be applied to Cu with binary eutectic solder. There exists no ternary compound between the two metastable phases.



In the metastable phase diagram, the tie-lines indicate the composition of two phases which are in metastable equilibrium. The difference between the diffusion rates in both phases are very large. Diffusion in liquid is much faster than in solid. The ratio of both liquid elements (Sn/Pb) at the liquid interface would be almost the same as the initial value. The intersection between the straight line that connects pure Cu and the liquid solder and the metastable Cu + liquid/liquid phase boundary is the composition of liquid at the interface. Moreover, the tie-line from the interface composition is directed towards Cu_6Sn_5 . This is applicable to other ternary systems such as Cu-Bi-Sn, Cu-Zn-Sn, etc.

(2) Prediction of Ti/Al₂O₃ interface reaction products by diffusion simulation



The calculated 1100°C isothermal section of Ti-Al-O system where intermetallic compounds, Ti₃Al, TiAl are shown. The metastable phase boundary is also shown. Before the formation of interface reaction product, interface β-Ti composition is somewhere on the metastable phase boundary. To determine exact interface composition, the first-forming phase should be estimated.

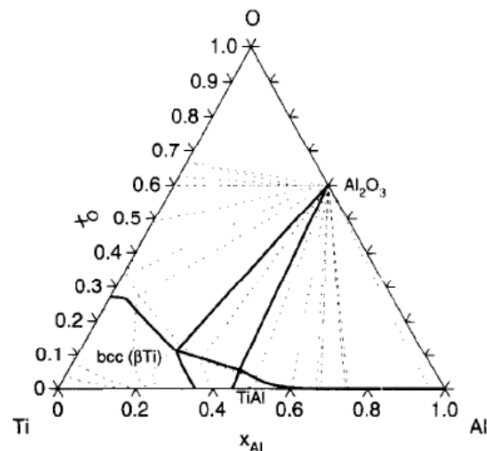
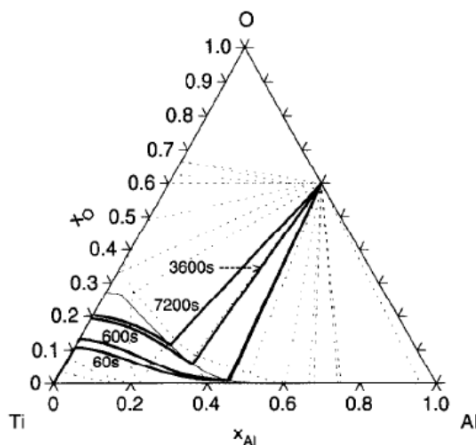
the diffusional fluxes of O and Al in the Ti.

$$J_O = -D_{OO}^n \nabla C_O - D_{OA}^n \nabla C_{Al}, \quad J_{Al} = -D_{AO}^n \nabla C_O - D_{AA}^n \nabla C_{Al}$$

the mobility of O and Al was assumed to be independent of each other's content. $D_{AO}^n = 0$, $D_{AA}^n = 0$.

$$J_O = -[RTM_O] \left[1 + \frac{d \ln f_O}{d \ln x_O} \right] \nabla C_O, \quad J_{Al} = -[RTM_{Ti,Al} + RTM_{Al,Ti}] x \left[1 + \frac{d \ln f_{Al}}{d \ln x_{Al}} \right] \nabla C_{Al}$$

after calculation, the mobility is the fastest for O and the lowest for Al.



Initial β-Ti is saturated with O, in 600s, and the sufficient diffusion ^{path} corresponds to isoactivity curve of O, but the interface composition is maintained.

after saturation of O in β-Ti, the interface composition is changed towards Al-poor and O-rich phase.

TiAl has strongest driving force, however, the interface composition is much Al-poor and the metastable phase boundary is located at Ti₃Al region.

If β-Ti thickness is sufficiently thin, the TiAl formed earlier would be changed to Ti₃Al.