

Growth Kinetics of the Intermetallic Layer at the Interface of Solid Metals with Liquid Soldering Alloys

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ABSTRACT

Mechanism and kinetics of formation of an intermetallic layer at the interface of a solid metal with a liquid solder are analyzed from a physico-chemical viewpoint. Mathematic equations allowing estimation of the thickness of an intermetallic layer under conditions of its dissolution in the solder melt are proposed. An example of calculations with the Ni_3Sn_4 intermetallic layer at the interface of nickel and a Pb-free Sn-base solder is presented.

INTRODUCTION

The formation of a brittle intermetallic layer weakens the transition zone between a solid metal and a solder. It is therefore essential in practice either to reduce its thickness to a permissible value or to avoid its occurrence at the solid-liquid interface at all. Conventionally, the intermetallic layer-growth kinetics are treated with the use of parabolic equations following from Fick's laws on the assumption of quasi-stationary distribution of the concentration of any component within growing layers [1].

However, if the solubility of a solid metal in a liquid soldering alloy is not zero, as is practically always the case, then the growth rate constant found experimentally proves time-dependent. Actually, it means that those equations do not provide an adequate description of the kinetics of the intermetallic layer-growth process for systems with a noticeable solubility in the liquid state, and hence the so-called growth law thus established is only valid under strict experimental or technological conditions, remaining unspecified in most cases. To overcome this drawback, in the framework of a physico-chemical analysis of the reaction-diffusion process in solid-liquid systems, a general three-term mathematic equation describing the intermetallic layer-growth kinetics under conditions of its simultaneous dissolution in a molten soldering alloy was derived [2]. The aim of this work is to show how this equation can be used to evaluate the layer thickness at the interface of a solid metal and a liquid solder in the course of the soldering process.

THEORY

Mechanism of intermetallic layer formation

Once formed, the A_pB_q layer grows at the interface between a solid metal A and a liquid solder B saturated with A at the expense of counter-diffusion of components A and B across its bulk followed by partial chemical reactions [2]

$$qB_{\text{diffusing}} + pA_{\text{surface}} = A_pB_q \quad (1)$$

and

$$pA_{\text{diffusing}} + qB_{\text{surface}} = A_pB_q. \quad (2)$$

These reactions yield the increases, dx_{B1} and dx_{A2} , in layer thickness during a time, dt , as shown in figure 1. Note that the initial stage in which A and B can react immediately is not considered.

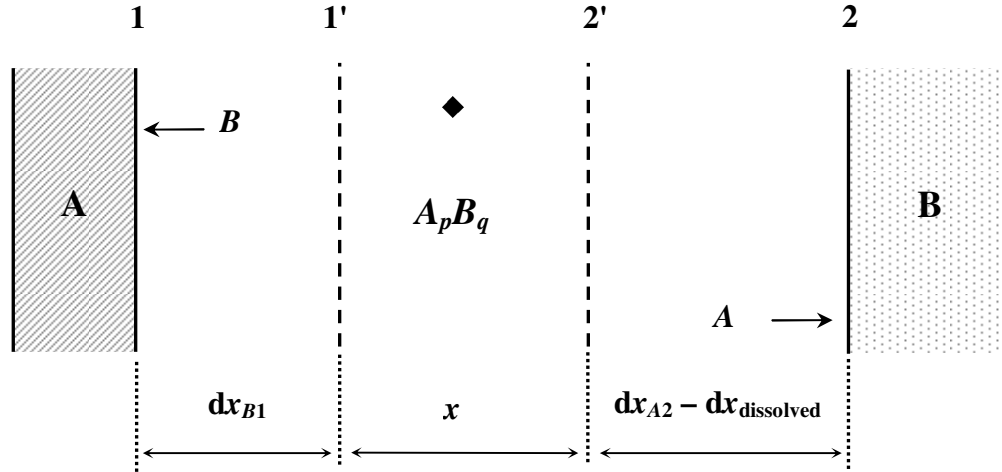


Figure 1. Schematic diagram to illustrate the mechanism of formation of the A_pB_q intermetallic layer under conditions of its simultaneous dissolution in the solder melt.

The layer growth rate is (for the derivation of this and other equations, see ref. [2])

$$\left(\frac{dx}{dt}\right)_{\text{growth}} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}}, \quad (3)$$

where k_{0B1} and k_{0A2} are chemical constants, k_{1B1} and k_{1A2} are diffusional constants. With the saturated solder melt, the layer-growth kinetics are initially linear at x up to 500-600 nm ($k_{0B1} \ll k_{1B1}/x$, $k_{0A2} \ll k_{1A2}/x$) and then parabolic at $x > \sim 1 \mu\text{m}$ ($k_{0B1} \gg k_{1B1}/x$, $k_{0A2} \gg k_{1A2}/x$).

The effect of dissolution on the layer growth rate

As seen in figure 1, in the case of the undersaturated solder melt the net rate of layer formation is the difference between the rates of its growth at interfaces 1 and 2 and dissolution at interface 2. The dissolution rate is

$$\left(\frac{dx}{dt}\right)_{\text{dissolution}} = b_t = b_0 \exp(-at), \quad (4)$$

where $b_0 = c_s k / \rho \varphi$, $a = ks/v$, c_s is the saturation concentration (solubility) of A in B at a given temperature, k is the dissolution rate constant, ρ is the density of the A_pB_q compound, φ is the

content of A in A_pB_q in mass fractions, s is the surface area of the solid in contact with the liquid, and v is the volume of the liquid.

A mathematical equation describing the growth kinetics of any intermetallic layer A_pB_q at the A - B interface under conditions of its simultaneous dissolution in the liquid phase is

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - b_0 \exp(-at). \quad (5)$$

It is clear that generally the layer growth is non-parabolic. Moreover, if

$$k_{0B1} + k_{0A2} < b_0 \quad (6)$$

(the sum of the rates of chemical reactions at the interfaces is less than the initial rate of dissolution), the A_pB_q layer does not form at the A - B interface. Strictly speaking, in such a case $k_{0B1} + k_{0A2}$ must be replaced by another constant k_0 characterizing the rate of direct reaction between A and B . As seen from equation 4, the dissolution rate diminishes exponentially from b_0 to b_t in the $0 - t$ time range. Hence, when

$$k_{0B1} + k_{0A2} = b_t, \quad (7)$$

the initially missing A_pB_q layer occurs at the A - B interface after some delay. At large t , $b_t \approx 0$, and the layer-growth kinetics become close to parabolic. Equation 5 cannot be solved precisely. However, its simpler forms can readily be employed in practice.

Growth of the A_pB_q layer at a constant dissolution rate

If the A_pB_q layer grows under conditions of diffusion control ($k_{0B1} \gg k_{1B1}/x$, $k_{0A2} \gg k_{1A2}/x$), while the dissolution rate is constant and equal to b_t , equation 5 reduces to

$$\frac{dx}{dt} = \frac{k_1}{x} - b_t, \quad (8)$$

where only one diffusional constant, k_1 , is retained for simplicity. In such a case, the layer thickness tends with passing time to a limiting value

$$x_{\max} = \frac{k_1}{b_t}, \quad (9)$$

that can be defined from the condition $k_1/x - b_t = 0$.

Equation 9 is suitable for estimating the thickness of the A_pB_q layer growing under conditions of its simultaneous dissolution in the liquid phase. The process of formation of the Ni_3Sn_4 intermetallic layer at the interface between solid nickel and a liquid 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb solder will be considered as an example.

EXPERIMENT

Electrolytic-grade nickel plates (99.98% Ni), tin (99.93% Sn), bismuth (99.999% Bi) and indium (99.999% In) slabs, and zinc granules (99.94% Zn) were employed for the investigation. With the saturated melts, experiments were carried out in a thermostat. The polished nickel plates, 14 mm × 5 mm × 3 mm, were mounted into graphite crucibles, with an inner diameter of 11 mm and a height of approximately 16 mm. The crucibles were placed in the thermostat at a required temperature. These were then filled with the flux from a moveable electric-resistance furnace, kept at the same temperature. After the temperature in the thermostat had equilibrated, the crucibles were filled with the metallic melt, previously saturated with nickel, from another moveable electric-resistance furnace also kept at the required temperature.

Nickel was allowed to react with the melt during a predetermined period of time in the 300-1800 s range. Then, the graphite crucibles with their contents were withdrawn from the thermostat and rapidly cooled down in water. Bimetallic specimens obtained were cut into two parts, normal to the long side of a nickel plate. The Ni-solder cross-sections were then prepared and examined with the help of metallography, X-ray analysis and electron probe microanalysis.

In the case of undersaturated melts, the rotating disc technique was employed (angular rotational speed $\omega = 24.0 \text{ rad s}^{-1}$). The disc surface area was 1 cm^2 . The amount of the solder material taken for each run was equivalent to a volume of the liquid phase of 10 cm^3 at a given temperature.

RESULTS AND DISCUSSION

Comparison of the Ni_3Sn_4 layer growth rate from the saturated and undersaturated melt

A single-phase intermetallic layer consisting of the Ni_3Sn_4 phase was found to form from both saturated and undersaturated melts at 250-450 °C. Two micrographs in figure 2 visualize the effect of dissolution on the growth rate of the Ni_3Sn_4 intermetallic layer at the Ni-solder interface. Dissolution is seen to produce almost a five-fold drop in layer thickness.

Note that under conditions of strong solder agitation at 250 °C and a dipping time of up to 600 s the Ni_3Sn_4 layer is missing from the interface of nickel and the undersaturated solder melt (figure 3). It provides evidence for the validity of equation 6.

Evaluation of the intermetallic layer thickness in the case of undersaturated solder melts

Calculations are carried out twice for each point t by putting in the denominator of equation 9 first equal to $(b_0 + b_t)/2$ and then b_t . Thus, two sets of the layer thickness are obtained. The first set represents the underestimated values, x_{under} . The second gives the overestimated ones, x_{over} . Clearly, experimental values, x_{exp} , must lie somewhere in between, as is indeed the case for the NiBi_3 [3] and Fe_2Al_5 [4] layers.

With a 87.5% Sn-7.5% Bi-3 %In-1% Zn-1% Sb solder and the Ni_3Sn_4 intermetallic layer (450 °C, $t = 2400 \text{ s}$, $\omega = 24.0 \text{ rad s}^{-1}$, $k = 6.2 \times 10^{-5} \text{ m s}^{-1}$, $c_s = 48.5 \text{ kg m}^{-3}$ [5], $s/\nu = 10 \text{ m}^{-1}$, $k_1 = 4.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $\rho = 8.68 \times 10^3 \text{ kg m}^{-3}$, $\phi = 0.27$), $x_{\text{under}} = 0.6 \text{ }\mu\text{m}$, $x_{\text{over}} = 1.5 \text{ }\mu\text{m}$, $x_{\text{exp}} = 1.2 \pm 0.2 \text{ }\mu\text{m}$. The agreement of these values appears to be quite sufficient for practical purposes to roughly estimate the intermetallic layer thickness at the solid-liquid interface.

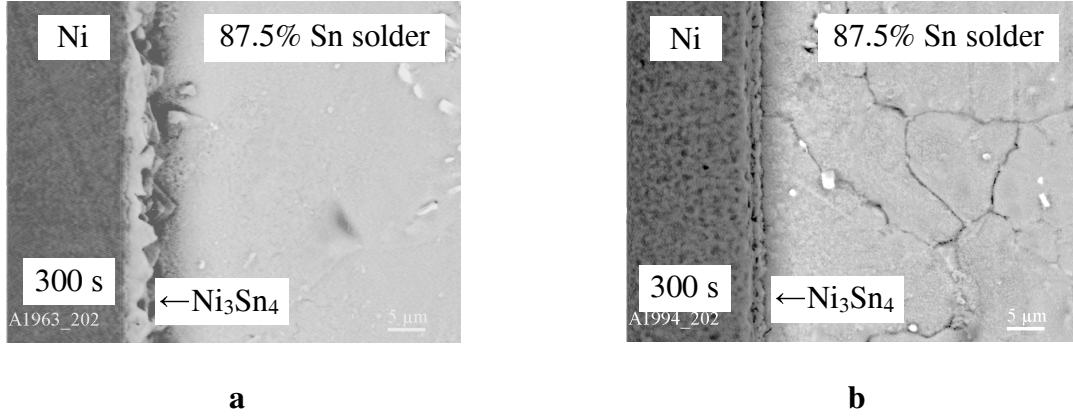


Figure 2. Transition zone between solid nickel and a liquid solder at 350 °C. (a) saturated melt; (b) undersaturated melt.

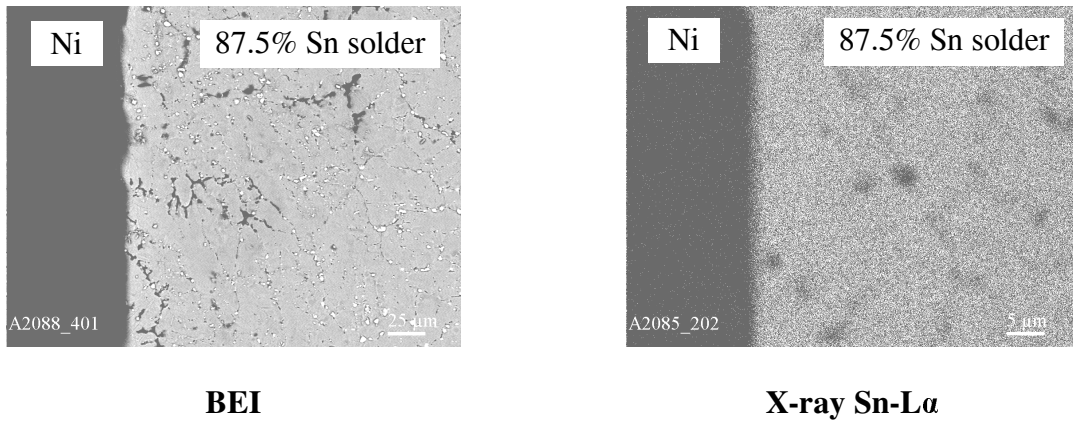


Figure 3. Backscattered electron image (BEI) and X-ray map of the transition zone formed between nickel and the undersaturated solder melt at a 250 °C and a dipping time of 600 s.

When employing equation 9, the main difficulty to overcome is evaluating the layer growth rate constant, k_1 . It can be done as follows.

1. If a single-phase intermetallic layer occurs in the case of both saturated and undersaturated melts, its value is found from the experimental thickness-time dependence for the saturated melt. In the case under consideration, this could only be done at small t because the thick Ni_3Sn_4 layers tend to destroy under the influence of the saturated solder melt at long holding times.

2. The layer growth rate constant, k_1 , is found from an experimental layer thickness-time dependence for the undersaturated melt using one or a few initial thickness values. Then, the other values can readily be calculated from equation 9, thereby reducing the amount of experimental work.

For example, in the case of the undersaturated 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb alloy melt at 350 °C, $k = 4.6 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 17.0 \text{ kg m}^{-3}$ (0.24% Ni in the soldering alloy) [5], $b_0 = 3.34 \times 10^{-6} \text{ m s}^{-1}$; ρ , φ and s/ν are as before. The experimental value, x_{exp} , of the Ni_3Sn_4 layer thickness at this temperature and a dipping time of 300 s is $1.0 \times 10^{-6} \text{ m}$. By assuming $x_{\text{exp}} = x_{\text{max}}$, one obtains from equation 9 $k_1 = x_{\text{max}} (b_0 + b_{300})/2 = 3.13 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

Note that the accuracy of this estimation is rather high, with the overestimated value of k_1 being $3.34 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and the underestimated one $2.91 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Comparison of calculated and experimental values of the Ni_3Sn_4 layer thickness is provided in table I. Again, the agreement is fairly well. It is also worth noting that the range in which the intermetallic layer thickness can vary is rather narrow, even though the time interval (600–2400 s) is relatively wide.

Table I. Calculated and experimental thicknesses of the Ni_3Sn_4 intermetallic layer grown from the undersaturated 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb solder melt at 350°C.

Time (s)	x_{under} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)	x_{over} ($\times 10^{-6} \text{ m}$)
600	1.06	1.1 ± 0.1	1.24
900	1.13	1.3 ± 0.1	1.42
1200	1.19	1.5 ± 0.2	1.63
1800	1.30	1.8 ± 0.2	2.14
2400	1.40	2.2 ± 0.3	2.82

3. If the data on the solid-state layer-growth rate are available, a value of k_1 can be estimated by extrapolation from the temperature dependence. Clearly, the temperature must not differ considerably in both cases. An example is calculations of the NiBi_3 layer thickness at the interface between nickel and bismuth or Bi-base alloys [3].

CONCLUSIONS

If the solubility of a solid metal in a liquid soldering alloy is appreciable, the effect of dissolution on the growth rate of an intermetallic layer must be taken into account. A general mathematic equation describing the layer growth kinetics under conditions of its simultaneous dissolution in a molten soldering alloy contains two positive terms and one negative term on its right-hand part. Application of proposed equations for estimating the intermetallic layer thickness at the solid metal-liquid solder interface yields satisfactory results.

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