

Effect of Dissolution on the Ni₃Sn₄ Growth Kinetics at the Interface of Ni and Liquid Sn-Base Solders

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Abstract. The Ni₃Sn₄ intermetallic layer occurs at the interface of nickel and the saturated or undersaturated Sn-base solder melt at 250-450 °C and dipping times of 300 to 2400 s. Mathematical equations are proposed to evaluate the thickness of the Ni₃Sn₄ layer formed under conditions of simultaneous dissolution in the undersaturated solder melt.

Introduction

During soldering of nickel with Sn-base solders, two physico-chemical processes, namely, dissolution of the solid metal in the liquid phase and formation of intermetallic-compound layers at their interface, take place simultaneously after wetting the solid metal surface with the molten solder. The occurrence of intermetallic compounds considerably deteriorates the mechanical strength of the transition zone between dissimilar materials. Usually, the intermetallics occur both at the phase interface between nickel and a Sn-base alloy in the form of a rather brittle continuous layer and in its vicinity in the melt material as the aggregation of relatively coarse grains. The former occurs in the course of a chemical reaction, while the latter forms either during cooling of the melt, or, in some cases, as a result of destroying the layer under the influence of the liquid phase.

If the main component of a solder is tin, intermetallic layers based on the Ni-Sn compounds may be expected to form at the Ni-solder interface in the course of soldering. Three intermetallic compounds Ni₃Sn, Ni₃Sn₂ and Ni₃Sn₄ are known to exist in the Ni-Sn binary system [1]. Though diffusional considerations [2] predict the simultaneous parabolic growth for the layers of all intermetallics available on an appropriate binary phase diagram, this does not always seem to be the case. More often, layer formation is sequential [3].

Conventionally, the intermetallic-layer growth kinetics are treated with the use of parabolic equations [2, 4-7]. 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. As a result, the parabolic 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.

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 mathematical equation describing the intermetallic layer-growth kinetics under conditions of its simultaneous dissolution in a molten soldering alloy was derived [3]. The main aim of this work is to show how to evaluate the effect of dissolution in the undersaturated solder melt on the Ni₃Sn₄ layer growth rate, using this equation.

Experimental

Materials and Specimens. Electrolytic-grade nickel plates (99.98%), tin (99.93%), bismuth (99.999%), indium (99.999%) and antimony (99.91%) slabs, and zinc granules (99.94%) were employed for the investigation. All contents are given in mass percent unless otherwise stated.

Nickel plates were re-melted in an electric-arc furnace to obtain 12-13 mm diameter rods. Cylindrical nickel specimens, 11.28 mm in diameter (1 cm^2 area) and 5.5 mm high, were machined from these rods for experiments with undersaturated solder melts. Sn-base soldering alloys were prepared by melting their components together in a specially designed device.

Experimental Methods. The growth process of intermetallic layers under conditions of their simultaneous dissolution in liquid solders of two compositions 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb and 80% Sn-15% Bi-3% In-1% Zn-1% Sb was studied in the temperature range 250-450 °C by the rotating disc technique (angular rotational speed, $\omega = 24.0 \text{ rad s}^{-1}$) using a rapid-quenching device [3]. Schematic diagram illustrating the growth and dissolution process of Ni_3Sn_4 in liquid soldering alloys is shown in Fig. 1.

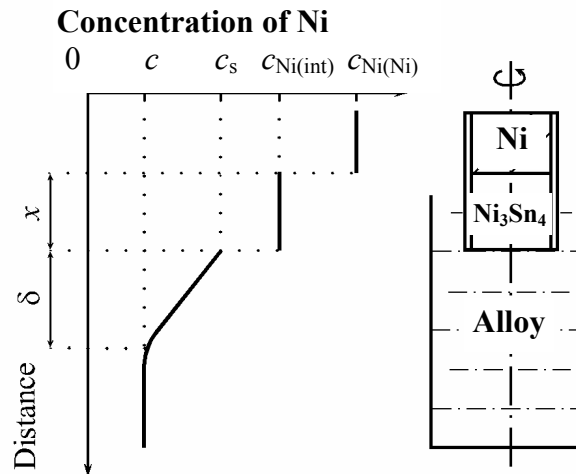


Fig. 1 Schematic diagram to illustrate the growth and dissolution process of the Ni_3Sn_4 intermetallic layer at the Ni-soldering alloy interface. c is the instantaneous concentration of nickel in a liquid solder, c_s is its solubility at a given temperature, $c_{\text{Ni(int)}}$ and $c_{\text{Ni(Ni)}}$ are concentrations of nickel in the intermetallic layer Ni_3Sn_4 and the nickel specimen, respectively, x is the thickness of the Ni_3Sn_4 layer, and δ is the thickness of the diffusion boundary layer at the solid-liquid interface. Not to scale.

The bimetallic nickel-solder sample obtained after the experiment was cut along the cylindrical axis using an electric-spark machine, ground flat and polished electrolytically using the "Elypovist" apparatus. The cross-sections prepared in this way were examined metallographically with the help of MIM-7 microscope equipped with a HP Photosmart 720 camera. X-ray patterns were taken on DRON-3 and URS-50 apparatus using CuK_α radiation. Electron probe microanalysis of the transition zone between nickel and Sn-base alloys was also carried out using a JEOL Superprobe-733 microanalyzer.

To investigate the growth process of intermetallic-compound layers from saturated melts, experiments were carried out in a steel thermostat. Polished nickel plates, $14 \text{ mm} \times 5 \text{ mm} \times 3 \text{ mm}$, were mounted into graphite crucibles. The crucibles were placed in the thermostat at a required temperature. These were then filled with the flux (eutectics of ZnCl_2 with NH_4Cl or KCl) 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, and 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 prepared and examined as described above.

Results and Discussion

To visualize the effect of dissolution on the process of intermetallic compound-layer formation at the interface between nickel and liquid solders, two sets of experiments were carried out. In the first set, the solder melt previously saturated with nickel was employed. Therefore, dissolution of the solid nickel in the liquid phase did not occur. In the second, the solder melt initially contained no nickel. Hence, the intermetallic layers were formed under conditions of their simultaneous dissolution in the solder melt, as shown in Fig. 1. In this case, the nickel disc was being rotated during the run at an angular speed of 24.0 rad s^{-1} .

Layer Phase Identity and Composition. With both solders, a single-phase intermetallic layer is formed from both saturated and undersaturated melts (Fig. 2). According to X-ray diffraction analysis (XRD), it consists of the Ni_3Sn_4 compound. XRD data were confirmed by electron probe microanalysis (EPMA).

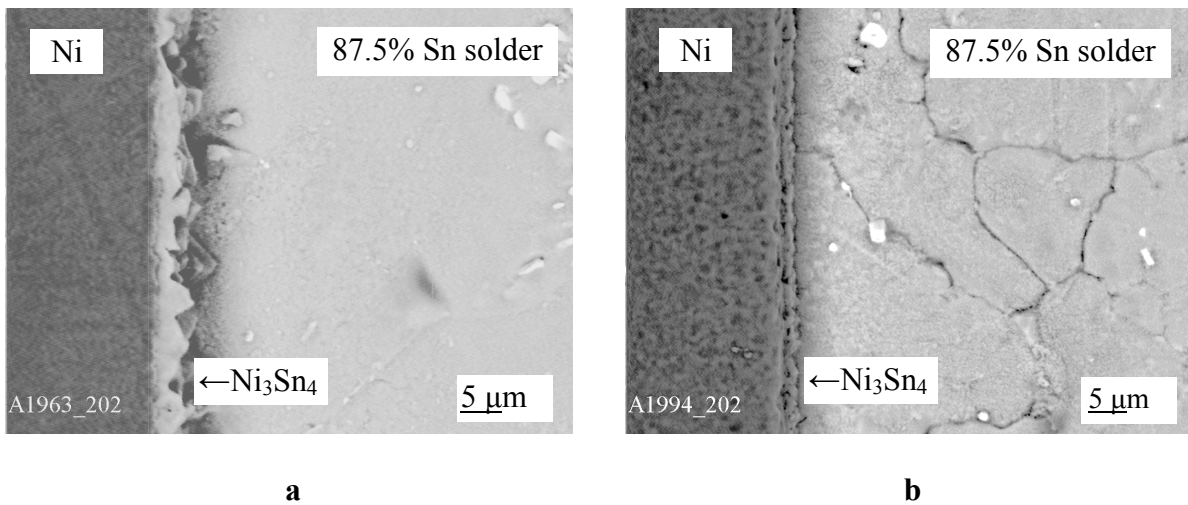


Fig. 2 Backscattered electron image of the transition zone formed between nickel and liquid soldering alloys at a temperature of 350°C and a dipping time of 300 s. (a) saturated melt, (b) undersaturated melt ($\omega = 24.0 \text{ rad s}^{-1}$).

EPMA measurements were carried out across the transition zone between nickel and soldering alloys. The phases revealed were Ni, Ni_3Sn_4 and the alloy taken for the experiment. No evidence of the presence of other Ni-Sn intermetallics at the nickel-solder interface was found.

Low content of bismuth (around 0.1 at.% with a 87.5% Sn solder and 0.2 at.% with a 80% Sn solder) in the the Ni_3Sn_4 layer is worth noting. The content of indium was 0.10-0.15 at.% with both solders, whereas zinc and antimony were practically absent from the intermetallic layer.

The Ni_3Sn_4 intermetallic layer tends to be destroyed under the influence of the liquid phase. This effect is typical of thick layers formed from saturated melts. Clearly, in such a case it is hardly possible to establish a reliable layer thickness-time dependence. Nonetheless, from Fig. 2 it is easy to notice that the Ni_3Sn_4 layer thickness is around 5 times less in the case of the undersaturated solder melt compared to the case of the saturated melt, other conditions being identical. Thus, the effect of dissolution on the layer growth kinetics at the Ni-solder interface is very appreciable.

Mechanism of Intermetallic Layer Formation. Generally, the Ni_3Sn_4 layer growth at the interface between nickel and a liquid Sn-base solder saturated with nickel at a given temperature is a result of counter-diffusion of nickel and tin atoms across its bulk followed by partial chemical reactions



These reactions yield the increases, $dx_{\text{Sn}1}$ and $dx_{\text{Ni}2}$, in layer thickness during a time, dt (Fig. 3).

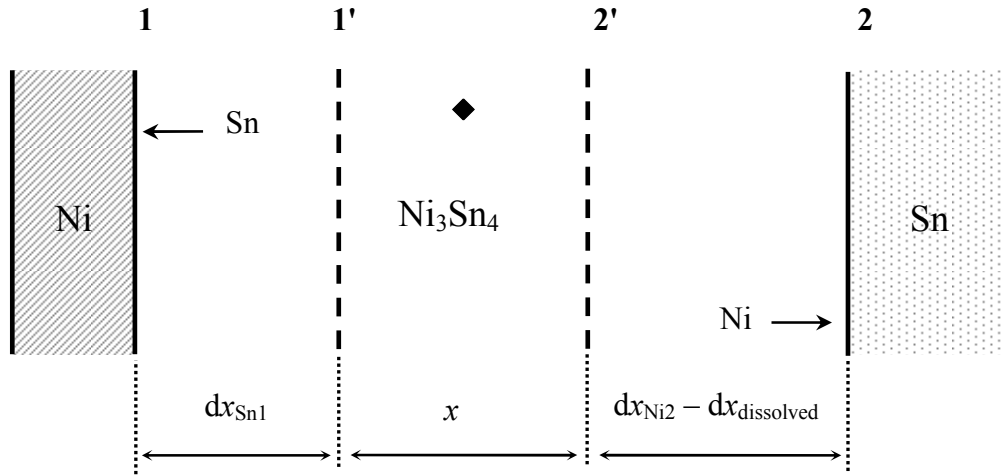


Fig. 3 Schematic diagram to illustrate the mechanism of formation of the Ni_3Sn_4 intermetallic layer under conditions of its simultaneous dissolution in the solder melt.

The layer-growth rate is [3]

$$\left(\frac{dx}{dt}\right)_{\text{growth}} = \frac{k_{0\text{Sn1}}}{1 + \frac{k_{0\text{Sn1}}x}{k_{1\text{Sn1}}}} + \frac{k_{0\text{Ni2}}}{1 + \frac{k_{0\text{Ni2}}x}{k_{1\text{Ni2}}}}, \quad (3)$$

where $k_{0\text{Sn1}}$ and $k_{0\text{Ni2}}$ are chemical constants, and $k_{1\text{Sn1}}$ and $k_{1\text{Ni2}}$ are diffusional constants (reaction-diffusion coefficients). With the saturated solder melt, the layer-growth kinetics must thus be initially linear and then parabolic.

Effect of Dissolution on the Intermetallic Layer Growth Rate. With 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 (see Fig. 3). The dissolution rate is

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

where $b_0 = c_s k / \rho_{\text{int}} \varphi$, $a = ks/v$, t is the time, c_s is solubility of nickel in a liquid solder at a given temperature, k is the dissolution rate constant, s is the surface area of the solid, and v is the volume of the liquid phase, ρ_{int} is the density of Ni_3Sn_4 , φ is the content of Ni in Ni_3Sn_4 .

A mathematical equation describing the growth kinetics of the Ni_3Sn_4 intermetallic layer at the Ni-solder interface under conditions of its simultaneous dissolution in the liquid phase is

$$\left(\frac{dx}{dt}\right)_{\text{growth}} = \frac{k_{0\text{Sn1}}}{1 + \frac{k_{0\text{Sn1}}x}{k_{1\text{Sn1}}}} + \frac{k_{0\text{Ni2}}}{1 + \frac{k_{0\text{Ni2}}x}{k_{1\text{Ni2}}}} - b_0 \exp(-at). \quad (5)$$

From Eq. (5), it follows that the layer growth is non-parabolic, excepting some particular cases. Moreover, if

$$k_{0\text{Sn1}} + k_{0\text{Ni2}} < b_0 \quad (6)$$

(sum of the rates of chemical reactions at interfaces 1 and 2 is less than the initial rate of dissolution interface 2), the intermetallic layer must be missing from the Ni-solder couple, as is the case for the Ni_3Sn_4 intermetallic layer at 250 °C and a dipping time of up to 600 s. Note that in this case the

reason for its absence from the initial couple is purely kinetic and not thermodynamic. Also, it is not connected with nucleating a new phase, as is often assumed, because even an already existing (artificially formed at the Ni-solder interface) intermetallic layer will inevitably disappear in the course of reaction, if the dissolution rate is constant and equal to b_0 .

From Eq. (4), it follows that at a constant ratio s/v the dissolution rate diminishes exponentially with increasing time from b_0 to b_t in the $0 - t$ time range. Hence, when

$$k_{0\text{Sn1}} + k_{0\text{Ni2}} = b_t \quad (7)$$

the Ni_3Sn_4 intermetallic layer must occur at the Ni-solder interface after some delay. At large t , b_t is practically zero 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 for evaluating the intermetallic-layer thickness.

Diffusional Growth of the Intermetallic Layer in the Case of a Constant Dissolution Rate. If the intermetallic layer grows under conditions of diffusion control ($k_{0\text{Sn1}} \gg k_{1\text{Sn1}}/x$, $k_{0\text{Ni2}} \gg k_{1\text{Ni2}}/x$), while the dissolution rate is constant and equal to b_t in the $0 - t$ time range, Eq. (5) reduces to

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

where only one diffusional constant, k_1 , is retained instead of the sum of two constants, $k_{1\text{Sn1}}$ and $k_{1\text{Ni2}}$, for simplicity. In such a case, the layer thickness tends with passing time to a limiting value

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

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

To estimate the effect of dissolution on the layer-growth rate, calculations of the thickness of the Ni_3Sn_4 layer grown from undersaturated solder melts are carried out twice for each point, t , by putting in the denominator of Eq. (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.

When employing Eq. (9), the main difficulty to overcome is evaluating the diffusional 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 layer thickness-time dependence for the saturated melt. For example, in the case of the saturated 87.5% Sn solder melt, the experimental value of the Ni_3Sn_4 layer thickness (whenever it has not been destroyed under the influence of the liquid phase) was found to be 1.6×10^{-5} m at 450 °C and a dipping time of 300 s. Hence, $k_1 = x^2/2t = 4.3 \times 10^{-13}$ m² s⁻¹. Other quantities necessary for calculations are $k = 6.2 \times 10^{-5}$ m s⁻¹ at $\omega = 24.0$ rad s⁻¹, $c_s = 48.5$ kg m⁻³ (0.69% Ni in the soldering alloy), $\rho_{\text{int}} = 8.68 \times 10^3$ kg m⁻³ [8], $\varphi = 0.27$, $s/v = 10$ m⁻¹, $b_0 = 1.28 \times 10^{-6}$ m s⁻¹. Using these data, one obtains the limiting values, $x_{\text{under}} = 0.6 \times 10^{-6}$ m and $x_{\text{over}} = 1.5 \times 10^{-6}$ m, for the thickness of the Ni_3Sn_4 layer grown from the undersaturated solder melt at 450 °C and a dipping time of 2400 s. The experimental value, x_{exp} , is $(1.2 \pm 0.2) \times 10^{-6}$ 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.

2. The layer growth-rate constant, k_1 , is found from an experimental thickness-time dependence for the undersaturated melt using one or a few initial thickness values. Then, the other values can readily be calculated from Eq. (9), thereby reducing the amount of experimental work. For example, in the case of the undersaturated 87.5% Sn solder melt at 350 °C, $k = 4.6 \times 10^{-5}$ m s⁻¹ at $\omega = 24.0$ rad s⁻¹, $c_s = 17.0$ kg m⁻³ (0.24% Ni in the soldering alloy), $b_0 = 3.34 \times 10^{-6}$ m s⁻¹, ρ_{int} , φ and s/v 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 1.0×10^{-6} m. By assuming $x_{\text{exp}} = x_{\text{max}}$, one obtains from Eq. (9) $k_1 = x_{\text{max}} (b_0 + b_{300})/2 = 3.13 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Comparison of calculated and experimental values of the Ni_3Sn_4 layer thickness is provided in Table 1.

Again, the agreement is fairly good. 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 1 Calculated, x_{under} and x_{over} , and experimental, x_{exp} , thicknesses of the Ni_3Sn_4 layer grown from undersaturated 87.5% Sn solder melts at 350°C ($\omega = 24.0 \text{ rad s}^{-1}$).

Time (s)	x_{under} ($\times 10^{-6}$ m)	x_{exp} ($\times 10^{-6}$ m)	x_{over} ($\times 10^{-6}$ 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 [9].

Summary

Mathematical equations proposed provides an adequate description of the Ni_3Sn_4 layer growth kinetics from undersaturated Sn-base solder melts.

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