

Briefly, the experimental procedure was as follows. To heat the materials under investigation to the required temperature and to maintain it, the electric-resistance furnace is employed. A flux is used both to pre-heat the solid specimen to the experimental temperature and to protect the melt from oxidation by atmospheric air. Before the experiment, the solid nickel specimen, 11.28 ± 0.02 mm in diameter (1 cm^2 area) and 5-6 mm high, is pressed into a graphite tube, 16 mm in diameter, to protect its lateral surface from the interaction with the melt. At the end of the run the nickel specimen is rapidly cooled down in a water bath located below the electric furnace. The melt material adhering to the surface of the nickel specimen is removed by melting in a muffle furnace and subsequent wiping. Then, the specimen is washed with water and alcohol, dried and weighed. Because the specimen had also been weighed before the run, its mass loss during dissolution in the melt could be determined. Samples of the alloys obtained after the runs were analyzed chemically to determine their nickel content. Nickel content was also found by electron probe microanalysis. The values obtained by these three methods were then averaged and used in further calculations.

THEORY

The Nernst-Shchukarev equation is known to describe the dissolution process of a solid in a liquid phase under conditions of sufficiently intensive agitation [11]. Its differential form is

$$\frac{dc}{dt} = k \frac{s}{v} (c_s - c), \quad (1)$$

where c is the instantaneous concentration of the dissolved substance in the liquid phase, t is the time, c_s is the solubility at a given temperature, k is the dissolution rate constant, s is the surface area of the solid, and v is the liquid volume. Integrated equation ($c = 0$ at $t = 0$) is

$$\ln \frac{c_s}{c_s - c} = k \frac{st}{v}. \quad (2)$$

Equations 1 and 2 indicate that the process of dissolution of a solid in a liquid is characterized by two quantities, namely, the solubility or saturation concentration, c_s , and the dissolution rate constant, k . If the pressure remains constant, the saturation concentration only depends upon temperature. The dissolution rate constant is in addition dependent upon the hydrodynamic conditions of flow of the liquid.

RESULTS AND DISCUSSION

Solubility of nickel in liquid soldering alloys

From equations 1 and 2, the concentration of the dissolved substance in the liquid is seen to increase with passing time and eventually to reach its limiting value, c_s , as was the case for the

nickel content in 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb and 80% Sn-15% Bi-3% In-1% Zn-1% Sb soldering alloys (figure 1).

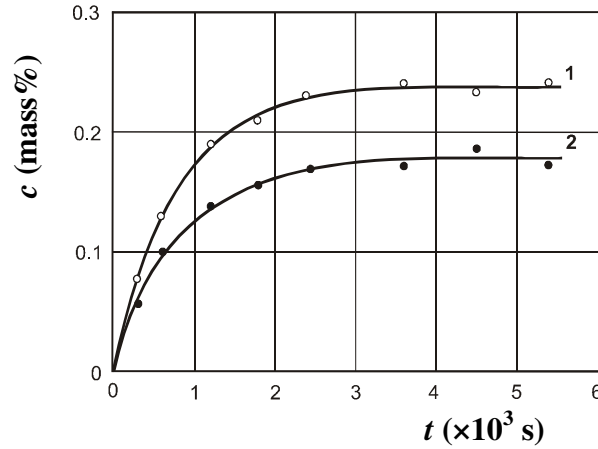


Figure 1. Nickel contents, dissolved into soldering alloys, are plotted against time to determine the solubility (saturation concentration), c_s . Rotational speed $\omega = 54.0 \text{ rad s}^{-1}$, $s/v = 27.5 \text{ m}^{-1}$. 1, 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb alloy; 2, 80% Sn-15% Bi-3% In-1% Zn-1% Sb alloy.

The temperature dependence of the solubility of nickel in the alloys was found to obey a relation of the Arrhenius type $c_s = A \exp(-E/RT)$, where A is the frequency factor, E is the activation energy (enthalpy of dissolution), R is the gas constant and T is the absolute temperature. The variation of $\ln c_s$ with $1/T$ is linear for both alloys (figure 2).

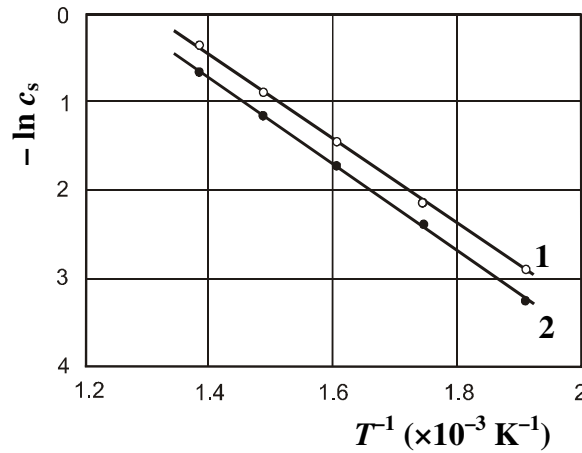


Figure 2. Temperature dependence of the solubility of nickel in liquid soldering alloys. 1, 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb alloy; 2, 80% Sn-15% Bi-3% In-1% Zn-1% Sb alloy.

Application of the least-squares fit method yielded the following equations:
 $c_s = 4.94 \times 10^2 \exp(-39500/RT) \%$ for a 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb alloy,
 $c_s = 4.19 \times 10^2 \exp(-40200/RT) \%$ for a 80% Sn-15% Bi-3% In-1% Zn-1% Sb alloy,
 where R is in $\text{J mol}^{-1} \text{K}^{-1}$ ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T in K. The linear regression coefficient is 0.99963 for the former alloy and 0.99969 for the latter.

Note that relatively small amounts of additives produce a very considerable effect on the solubility of nickel in Sn-base soldering alloys. The temperature dependence of the nickel solubility in pure tin at 300-700 °C is reported to obey the equation [12] $c_s = 5.34 \times 10^2 \exp(-36900/RT)$ %.

Comparison of the solubility values calculated from these three temperature dependences is provided in table I. Twenty percent of additives (Bi, In, Zn and Sb) are seen to produce more than a two-fold decrease in nickel solubility values. Such a large drop could not be expected judging from the solubility values in binary systems of nickel with the main alloy constituents tin and bismuth. For example, at 350 °C c_s is 0.43% Ni for tin [12] and 0.39% Ni for bismuth [13]. In view of their relatively low content in the alloys, the influence of indium, zinc and antimony can hardly be significant. Note that for a similar alloy containing 51% Bi, 42% Sn, 5% In and 2% Zn the nickel solubility at 350 °C is much lower, namely, 0.015% [13]. These data provide evidence that the solubility values decrease as the alloy composition approaches from both sides to the composition of the binary eutectic Bi-Sn (57% Bi and 43% Sn [9]). It still remains to find out whether this trend is only characteristic of the system investigated or of others as well.

Table I. Solubility, c_s , and dissolution rate constant, k , of nickel in Sn-base soldering alloys.

Temperature (° C)	c_s (%)			k ($\times 10^{-5} \text{ m s}^{-1}$)	
	100% Sn [12]	87.5% Sn...	80% Sn...	87.5% Sn...	80% Sn...
250	0.11	0.056	0.040	1.3	1.1
300	0.23	0.12	0.091	2.7	2.6
350	0.43	0.24	0.18	4.6	4.5
400	0.73	0.42	0.32	5.4	5.3
450	1.15	0.69	0.52	6.2	6.1

Dissolution rate constants

Besides the solubility, c_s , another main characteristic of the dissolution process of a solid metal in a liquid solder is the dissolution rate constant, k . To obtain an accurate measure of this constant, the initials parts of the dissolution curves such as those shown in figure 1 were investigated in detail at an angular disc rotational speed of 24.0 rad s⁻¹. The linearity of a plot of $\ln [c_s/(c_s - c)]$ against st/v in figure 3 provides evidence for the validity of equations 1 and 2, which can thus be used to determine accurate values of the dissolution rate constant.

Experimental values of the dissolution rate constant at a disc rotational speed of 24.0 rad s⁻¹ are included in table I. Dissolution rate constants obtained at 350 °C and other rotational speeds are presented in table 2. The mean relative error of their determination is $\pm 8\%$.

Note that, although the solubility values of nickel in the alloys at a given temperature differ considerably, appropriate dissolution rate constants are very close. This appears to be a general trend in the dissolution of transition metals and their alloys in liquid-metal melts. It means that, in spite of the great difference in solubility values, the rates, with which those are attained, are not so different. Although the former may differ by a few orders of magnitude, the

latter usually fall in the range $(1-10) \times 10^{-5} \text{ m s}^{-1}$ at reasonable rates of agitation of the liquid [11-14].

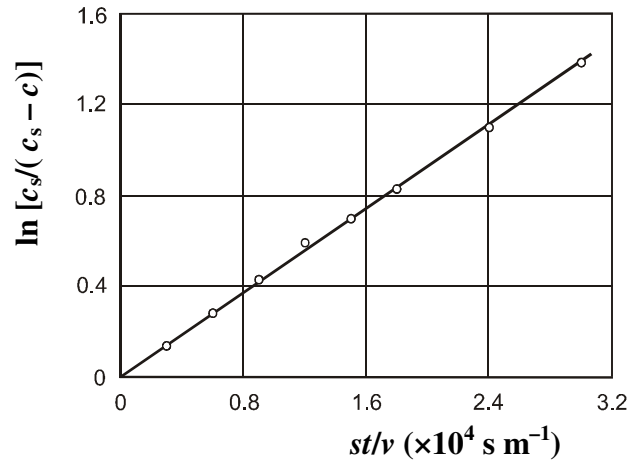


Figure 3. A plot of $\ln [c_s / (c_s - c)]$ against st/v for a liquid 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb alloy at a temperature of 350 °C. Disc rotational speed $\omega = 24.0 \text{ rad s}^{-1}$, $s/v = 10.0 \text{ m}^{-1}$.

Table II. Dissolution rate constants, k , of nickel in Sn-base soldering alloys at 350 °C and disc rotational speeds in the range 6.45-82.4 rad s^{-1} .

$\omega (\text{rad s}^{-1})$		6.45	9.00	15.3	24.0	32.7	54.0	82.4
$k (\times 10^{-5} \text{ m s}^{-1})$	87.5% Sn...	2.6	2.9	3.9	4.6	5.8	7.0	9.0
	80% Sn...	2.4	3.1	3.7	4.5	5.2	7.3	8.8

Dissolved portion of nickel in contact with solders

The data presented can readily be used to estimate the thickness, x_d , of the dissolved portion of the solid nickel material during soldering:

$$x_d = c_s k t / \rho_{\text{Ni}}, \quad (7)$$

where ρ_{Ni} is the density of nickel, kg m^{-3} , and c_s must be expressed in kg m^{-3} .

Note that this value is not so small, especially from the point of view of microelectronics. For a 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb solder at a temperature of 250 °C, with $c_s = 4.0 \text{ kg m}^{-3}$, $k = 0.1 \times 10^{-5} \text{ m s}^{-1}$ (very slight convective agitation of the solder melt) and $t = 10 \text{ s}$, it is equal to 4.5 nm. At 350 °C and the same values of k and t , it increases to 19 nm.

CONCLUSIONS

The dissolution process of nickel in liquid 87.5% Sn-7.5% Bi-3% In-1% Zn-1% Sb and 80% Sn-15% Bi-3% In-1% Zn-1% Sb soldering alloys is characterized by the solubility, c_s , and the dissolution rate constant, k . The temperature dependence of the solubility of nickel in those alloys is described in the 250–450 °C range by an equation of the Arrhenius type $c_s = A \exp(-E/RT)$, where $A = 4.94 \times 10^2 \%$ and $E = 39.5 \text{ kJ mol}^{-1}$ for the former alloy and $A = 4.19 \times 10^2 \%$ and $E = 40.2 \text{ kJ mol}^{-1}$ for the latter. In spite of the great difference in solubility values, appropriate dissolution rate constants of nickel are rather close for both soldering alloys. The data presented can be used to evaluate (i) the thickness of the dissolved portion of the solid nickel material during soldering, (ii) the extent of saturation of a solder with nickel and (iii) the effect of dissolution on the growth rate of intermetallic layers at the Ni-solder interface.

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