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Osaka University
Reaction of Iron-based Alloys with Molten Lead-free Solder†

Tadashi TAKEMOTO * and Masaharu TAKEMOTO **

Abstract

The reaction between molten lead-free solder and iron-based alloys has been investigated by evaluating the dissolution rate of iron-based alloys in molten solders. The dissolution rate of these alloys used for plating on the tips of soldering irons and container materials of soldering baths are about three times larger when tested in lead-free solder than in conventional Sn-Pb eutectic, which indicates that the iron plating of soldering iron tips and container materials for soldering baths are subject to heavy damage in lead-free solders than in Sn-Pb eutectic. The rate showed little dependence on iron based alloy composition. Homogeneous dissolution was observed in all specimens including alloyed steels. A decrease in reaction temperature and time and a small addition of iron into solder were found to be effective for the suppression of dissolution.

KEY WORDS: (Lead-free Solder), (Dissolution of Iron), (Soldering iron tip), (Iron-based Alloy), (Stainless Steel), (Soldering)

1. Introduction

Lead-free soldering has been proceeding as an environmentally conscious technology under consideration of the ban of lead by EU Directive on Waste Electric and Electronic Equipments (WEEE) and Restrictions of Hazardous Substances (RoHS)\(^1\). Many manufacturing companies in Japan have already completed their feasibility studies, and they are now sending a variety of products on the market. The major lead-free solder system substitution for the conventional Sn-Pb eutectic is the Sn-Ag-Cu family\(^2,3\), however, the history of lead-free solders is quite short, and there is not sufficient accumulation of data corresponding to the various conditions in market use.

For example, lead-free solders show large dissolution rate of copper at soldering temperatures\(^4\). If this characteristic is reflected by the other materials, the materials contacting molten lead-free solder will also be severely dissolved into molten lead-free solder, and the phenomena can be called erosion\(^5,6\). The soldering iron is an important tool in manual soldering. The tip of a soldering iron consists of bulk Cu and Fe surface plating to protect erosion of Cu into molten solder. The Fe plating plays an important role to avoid erosion of Cu and it also transfers heat to both solder and soldering pads. For this purpose, the surface of plated Fe should usually wet with molten solder to transfer the heat sufficiently and quickly to the materials to be soldered. Accordingly, investigation of the reaction rate between Fe and molten solder is quite important to establish the endurance of Fe plating on soldering irons in contact with molten lead-free solder. However, there is little precise data about this reaction. Accordingly, the work aimed to clarify the reaction between iron-based alloys and molten lead-free solder.

2. Materials and Experimental

To investigate the reaction between molten solder and iron-based alloys, fine iron based wires were vertically immersed into molten solder maintained at a constant temperature, Fig. 1. The test temperature was measured by a sheathed thermocouple immersed in molten solder. A graphite crucible was used as a container for the molten solder. After immersion for predetermined periods, the cross section of the wire was measured. The reaction proceeded almost homogeneously from the surface, and the reaction rate was measured as dissolution thickness according to the following equation.

\[ r_d = (d_0 - d)/2 \]

Where,

- \( r_d \): Dissolution thickness
- \( d_0 \): Initial diameter of iron-based wire
- \( d \) : Diameter after immersion test of iron-based wire

As can be easily understood, the dissolution thickness corresponds to the reduction of radius after the immersion test.

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**Fig. 1** Schematic of apparatus for measuring dissolution of fine iron based wires in molten solder.

**Table 2** Nominal chemical compositions in mass% and melting temperature range of solders used for dissolution test.

<table>
<thead>
<tr>
<th>Solder composition</th>
<th>Symbol</th>
<th>Liquidus (K)</th>
<th>Solidus (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.5Ag</td>
<td>SA</td>
<td>494</td>
<td>494</td>
</tr>
<tr>
<td>Sn-37Pb</td>
<td>SP</td>
<td>456</td>
<td>456</td>
</tr>
</tbody>
</table>

Table 1 shows the chemical compositions of iron based alloys used for the dissolution test. The fine wire with diameter of 0.9 mm was used. Three alloyed steels were used to clarify the possibility of reduction of reaction by addition of several alloying elements such as C, Si and Mn. Prior to immersion, the surface of the wire was slightly scrubbed by emery paper of 1000 grade to remove oxide. After ultrasonic cleaning in an acetone bath, soldering flux was supplied to the specimen surface before immersion into molten solder.

Table 2 shows the nominal chemical compositions and melting temperature ranges of solders used for the dissolution test. The conventional Sn-37Pb eutectic solder was used for comparison. Taking into consideration of the tip temperature used for manual soldering, the test temperatures for dissolution test were chosen from 623K to 723K which were relatively higher than the usual soldering temperature.

3. Results

3.1 Dissolution of pure Fe

Figures 2(a) and 2(b) show the effect of temperature and time on the dissolution thickness of pure iron in molten Sn-3.5Ag and Sn-37Pb respectively. In both figures, the relatively large scattering of data can be seen, however, it is clear that the dissolution thickness increased with increasing the test temperature and holding time. The dissolution reaction is considered to be controlled by diffusion, however, the dissolution thickness seems to increase linearly with holding time. The reason is not clear, however, the convection flow in the crucible may be relatively strong. The severe convection flow brings the dissolved iron far away from the specimen surface eliminating the saturated layer at the solder/Fe interface. This may enhance the dissolution rate of fine Fe wire resulting in the linear relation between dissolution rate and holding time. In fact, there are several examples that show linear relationships between dissolution rate and holding time, they are dissolution of Ag, Au, Cu in molten Pb-5Sn 2.5Ag and Pb-5Sn3 and various metals in molten Sb-Pb.

The other important result in Fig. 2 is that molten Sn-3.5Ag solder shows an almost 3 to 4 times larger dissolution rate than in Sn-37Pb. The reduction of cross

**Table 1** Chemical compositions and diameter of iron based alloys used for dissolution test.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Diameter (mm)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Fe</td>
<td>0.9</td>
<td>0.0046</td>
<td>0.01</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>FM</td>
<td>0.9</td>
<td>0.10</td>
<td>0.88</td>
<td>1.48</td>
<td>-</td>
<td>0.01</td>
<td>0.015</td>
<td>0.012</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe6C</td>
<td>0.9</td>
<td>0.64</td>
<td>0.21</td>
<td>0.49</td>
<td>-</td>
<td>-</td>
<td>0.011</td>
<td>0.012</td>
<td>Bal.</td>
</tr>
<tr>
<td>F9C</td>
<td>0.9</td>
<td>0.98</td>
<td>0.2</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.007</td>
<td>Bal.</td>
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</table>
section in Sn-3.5Ag is evident after immersion for 8h at 723K in Fig. 3. As mentioned earlier, the round cross section is observed showing dissolution proceeded homogeneously. The Fe plating on a soldering iron tip is expected to have more severe damage in Sn-3.5Ag than in the conventional Sn-37Pb.

3.2 Dissolution of alloyed steels

The dissolution rates of several alloyed steels were investigated at 723K and 673K using Sn-3.5Ag solder. Figure 4 shows the results at 723K. Similar to Fig. 2, large scattering was also observed, however, there seems no clear difference in dissolution thickness among the alloyed steels. Only a slight difference may exist between pure Fe and alloyed steels. Pure iron seems to show slightly lower dissolution rates. A similar tendency was also observed in the test at 673K. To avoid complexity, each data point at 673K is not plotted in Fig. 4, however, the figure indicates the range of dissolution thickness for alloyed steels and the line representing mean value for pure Fe is indicated. The data for pure Fe is slightly lower than in alloyed steels. The results show that the dissolution of Fe cannot be suppressed by the use of alloyed steels with small amounts of C, Si and Mn. Figure 5 shows the cross section of alloyed steels after immersion at 723K for 8h. Similar to pure Fe specimens, round cross sections were observed in all alloyed steel specimens indicating homogeneous dissolution.

4. Discussion

The present study revealed a higher dissolution rate of iron based materials in Sn-3.5Ag lead-free solder than in Sn-37Pb conventional solder. The results suggest that the Fe plating on soldering iron tips used for Sn-Ag based lead-free solders is subjected to more severe conditions than in Sn-Pb solders.

The dissolution reaction of solid metals and alloys into molten solder can be expressed by the following equation:

$$\frac{dC}{dt} = \frac{K}{V}(C_s-C)$$

(1)

where, $C$ : Concentration of solute in liquid after reaction time $t$ (s)

$K$ : A constant

$A$ : Interfacial area between solid and liquid

$V$ : Volume of liquid

$C_s$ : Saturation concentration of solute in liquid

The values of $A$ and $V$ are constants in this study, therefore, an increase of $(C_s-C)$ in Eq. (1) enhances dissolution. The concentration difference $(C_s-C)$ can be considered as a driving force for dissolution. The volume of solder can be recognized as sufficiently large when compared with the surface area of a fine wire, therefore, $C$ in Eq. (1) can be regarded as a constant. Accordingly, an increase of $C_s$, a larger saturation concentration, drives enhanced dissolution which corresponds to the rise of test temperature.

From this point, pre-addition of Fe in Sn-3.5Ag solder reduces the concentration difference $(C_s-C)$ which
Table 3 Effect of addition of Fe in Sn-3.5Ag on suppression of dissolution thickness of pure Fe, μm.

<table>
<thead>
<tr>
<th>Solder</th>
<th>Test time (h)</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.5Ag</td>
<td>Min.</td>
<td>54.5</td>
<td>103.5</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>73.5</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>63.2</td>
<td>114</td>
</tr>
<tr>
<td>Sn-3.5Ag-0.050Fe</td>
<td>Min.</td>
<td>13</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>19</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>15.2</td>
<td>23.1</td>
</tr>
</tbody>
</table>

![Sn-3.5Ag and Sn-3.5Ag-0.015Fe](image)

**Fig. 6** Cross section of pure Fe after dissolution test at 723K for 8h.

is also expected to reduce the dissolution rate, judging from Eq. (1). According to the liquidus line in the Sn-Fe binary system\(^{[12]}\), the saturation concentration of Fe in molten Sn at 723K is about 0.05mass%. The dissolution test of pure Fe in Sn-3.5Ag-0.05Fe solder was conducted at 723K for up to 8h. Table 3 shows the results of the dissolution test. In both test periods, the dissolution of pure Fe was drastically suppressed by the addition of 0.05Fe in Sn-3.5Ag. The dissolution thickness of the Fe-added solder was less than 1/4 that of the Sn-3.5Ag.

Figure 6 shows the cross section of specimen tested in Sn-3.5Ag-0.05Fe solder at 723K for 8h. It is evident that the dissolution was sufficiently suppressed by addition of 0.05mass%Fe to Sn-3.5Ag. The formation of a relatively thick reaction layer was observed in Fe-added solder, whereas the formation was quite thin in Sn-3.5Ag. The layer can be recognized as FeSn\(_2\) from the compositional analysis by WDX, (Wave Dispersive characteristic X-ray analysis), which corresponds to the phase estimated from the Sn-Fe binary phase diagram. The formation of this layer protected further dissolution of Fe to molten solder, however, the formation of such layer may not be preferable from the view point of solderability of the soldering iron tip. The formed layer may reduce the wettability of the soldering iron tip to some extent. It is better that the additional amount of Fe should correspond to the saturation concentration at the operation temperature. The value can be easily determined by the liquidus curve from the literature\(^{[12]}\).

The wettability of the solder containing Fe showed a similar wetting area and therefore a similar contact angle to solder without Fe. Figure 7 shows the results of spread tests at 523K for 30s in a homogeneous heating chamber using ultra red heat source. The spread area and contact angle show similar values in both solders. Of course the liquidus of Fe added solder becomes quite high according to the added amount of Fe, however, wettability and appearance were maintained almost the same after the spread test was conducted at lower temperatures than the liquidus. It is confirmed that the addition of Fe of saturated concentration at the operating temperature to solder is quite effective in suppressing the dissolution of Fe without the decrease of wettability. The phenomenon is quite similar to the addition of Ag to solder to inhibit silver scavenging\(^{[13]}\). And the addition of Cu to Sn-Pb to reduce the dissolution rate of Cu fine wire\(^{[14]}\).

![Arrhenius plots](image)

**Fig. 8** Arrhenius plots of dissolution rate of pure Fe in Sn-37Pb and Sn-3.5Ag respectively.

One of the simple explanations for the high dissolution rate of lead-free solder can be explained by using the concentration difference (C\(_{\text{eq}}\)-C) in Eq. (1). In lead-free solder, the high Sn content increases (C\(_{\text{eq}}\)-C) at soldering temperature, and therefore, the increment of Sn is responsible for the high dissolution rate of Sn-based lead-free solder.

The dissolution thickness measured after the immersion test showed relatively large scattering, however, the plots between the dissolution thickness and holding time showed linear relation at each test temperature. The dissolution rate can be determined
according to the slope of the plots shown in Fig. 2. The logarithm of the dissolution rate, $k$ in $\mu$m/h, was plotted against the inverse of test temperature, $1/T$, $T$ in K, Fig. 8. Figure 8 shows the so called Arrhenius plots for dissolution rate of Fe in molten Sn-3.5Ag and Sn-37Pb. The plots showed good linearity for both solder. The apparent activation energies can be calculated from the slope of the plots, as 68.8kJ/mol for Sn-3.5Ag and 64.4kJ/mol for Sn-37Pb respectively. The activation energy for self-diffusion of Sn in molten Sn is 16.7kJ/mol\cite{15}, and the activation energy for impurity diffusion of Sn in $\alpha$-Fe is 221-232kJ/mol\cite{15,16}.

The experimentally obtained values in this experiment stand between these values. The obtained values are about 1/3 of the impurity diffusion of Sn in $\alpha$-Fe. The value is usually assumed to indicate that the reaction rate is controlled by grain boundary diffusion, however, no apparent grain boundary diffusion in Fe wire was observed in cross sectional observation. The diffusion within the reaction layer may influence on the rate controlling process of this system.

5. Conclusions

The reaction between iron based alloys and lead-free solder was investigated in relation to the test temperature and time by measuring the dissolution thickness of fine wire in molten solder. The main results obtained are summarized as follows.

(1) The dissolution of iron based alloys does occur during immersion in molten solder. The dissolution thickness increases with an increase of holding temperature and time.

(2) Sn-3.5Ag lead-free solder showed almost 3 ~ 4 times higher dissolution rates than in the conventionally used Sn-37Pb.

(3) Addition of Fe with saturated concentration at the test temperature drastically reduced the dissolution rate, the phenomenon can be interpreted from the basic equation for dissolution. The addition of 0.05mass%Fe was found to be effective in suppressing the dissolution rate of Fe into Sn-3.5Ag at 723K.

(4) The apparent activation energies for dissolution of pure Fe in molten solders were 68.8kJ/mol for Sn-3.5Ag and 64.4kJ/mol for Sn-37Pb respectively. These values were about 1/3 of the activation energy of impurity diffusion of Sn in $\alpha$-Fe.

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