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Effect of Nd and La on surface tension and wettability of Sn-8Zn-3Bi solders①

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Abstract: Maximum bubble pressure measurement was employed to evaluate surface tension of Sn-8Zn-3Bi-(0－0.15)Nd and Sn-8Zn-3Bi-(0－0.15)La solder melts. Wetting balance method was used to measure wetting force and wetting time on Cu substrate of the two group solders. The experimental results show that minute amount of Nd or La addition to Sn-8Zn-3Bi solder causes significant decrease of the surface tension of the solder melts at 200－240 ℃ and Nd addition is more effective on reduction of surface tension than that of La. Nd or La addition has the effect on enhancing the wetting force of the solder melts on Cu substrate, which results from the decrease of interfacial tension between the solder melt and Cu substrate. The wetting force reaches the maximum when 0.1% Nd is added to the base alloy. The contact angle between Sn-8Zn-3Bi base solders and Cu substrate decreases with the addition of Nd or La and the minimum of the contact angle is obtained from the solder with 0.1% Nd addition.

Key words: lead-free solder; zinc; neodymium; lanthanum; surface tension; wettability
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1 INTRODUCTION

With increasing global concern on environment and health, more and more attention has been paid to suitable substitution of lead-free solders for Sn-Pb solders. The most widely recommended lead-free solders can be divided into Sn-Ag system, Sn-Cu system, Sn-Zn system, Sn-Bi system and Sn-In system. Even though the main stream of the lead-free alloys is the alloy based on the Sn-Ag-Cu system, this alloy has high melting point up to 217 ℃, resulting in the increase of soldering temperature[1－3].

Sn-Zn eutectic alloy has recently been considered a candidate for lead-free solder material because of its low melting point (198 ℃), excellent mechanical properties and low cost. However, since Zn-contained alloys have the problem of oxidation and poor wetting[4－6], new Sn-Zn based alloys are still under development. Lin et al[7, 8] have reported that adding Ag or Al to Sn-9Zn alloys can accelerate their wetting on Cu substrate. Yu et al[9] and Xie et al[10] have demonstrated the effect of Re and Cu on the wetting behavior on Cu substrate of Sn-Zn based solders. The wettability of Sn-9Zn base alloys can be improved with addition of Ce-La mistch metal or Cu. Chen et al[11] have reported wetting behavior of Sn-Zn-Ga alloys, and revealed that addition of Ga can enhance the wetting area on Cu. The patent[12], Kim et al[13] and Zhou et al[14] have reported that Bi as a surface-active element can develop wettability of Sn-Zn solders. A series of researches are thus underway to improve wettability of Sn-Zn based alloys, and a lot of alloying elements have been widely discussed. Surface tension of solder melt and interfacial tension between solder melt and Cu are two important factors which determine its wetting behavior. But there is not enough discussion on relationship between alloying elements and surface tension or interfacial tension with Cu substrate of Sn-Zn based alloys.

The objective of this study is to display the effect of the forth additives(Nd and La) on the surface tension and the wettability of Sn-8Zn-3Bi solders. The focus is placed on deciding a more effective element which can reduce the surface tension and the interfacial tension on Cu substrate of the solders.

2 EXPERIMENTAL

2.1 Materials

Elements with industrial purity were used to prepare alloys in this study. Sn-5Nd and Sn-5La master alloy ingots were firstly prepared by melting Sn and Nd or Sn and La in N_2 atmosphere at 720 ℃ for 20 min. Then, these master alloys were remelted with Sn, Zn and Bi in N_2 atmosphere at 400 ℃. After insulation for 10 min, the melts were

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chill casted as ingots in a steel mold. The final composition was controlled by inductively coupled plasma (ICP). The designed chemical compositions of these alloys are given in Table 1. Alloy 1 was the base alloy. Different amounts (from 0.05% to 0.15%, mass fraction) of Nd were added into alloys 2, 3 and 4, and different amounts (from 0.05% to 0.15%, mass fraction) of La were added into alloys 5, 6 and 7.

Table 1 Designed chemical compositions of alloys (mass fraction, %)

Alloy No	Zn	Bi	Nd	La	Sn
1	8	3	–	–	Bal
2	8	3	0.05	–	Bal
3	8	3	0.10	–	Bal
4	8	3	0.15	–	Bal
5	8	3	–	0.05	Bal
6	8	3	–	0.10	Bal
7	8	3	–	0.15	Bal

2.2 Experimental principles and methods

Fig. 1 shows the apparatus of surface tension measurement. The apparatus included a heater, a thermocouple, a WT-80 temperature controller, a tubule with 1.0 mm inside radius, a pressure controller and a pressure gauge.

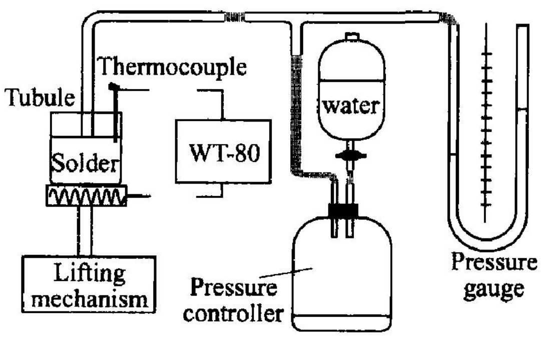

Fig. 1 Apparatus of surface tension measurement

The end of the tubule was just immerged in melting solder. Fig. 2 shows the process of forming a bubble. At the end of the tubule, curvature radius(r) of the bubble decreased firstly with the increase of pressure difference (Δp) between inside and outside of the bubble. After r reached the radius of the tubule (R), r increased with the volume increase of the bubble, and Δp decreased. So the following relation could be proposed by Laplace formula:

$$\Delta p_{max} = 2\sigma/R \quad (1)$$

where σ was the surface tension of the melt.

If the end of the tubule was just immerged in

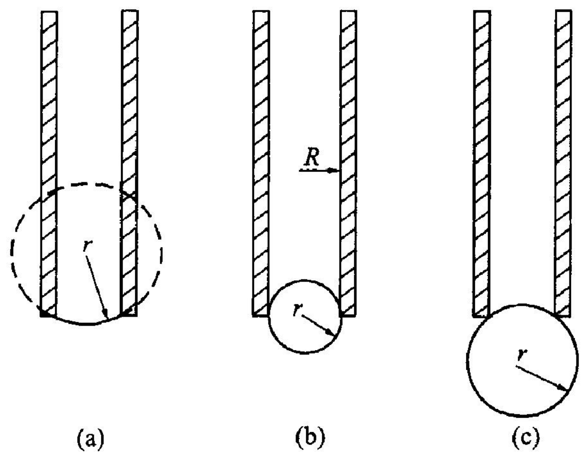

Fig. 2 Schematic diagram of bubble in forming

the melting solder, Δp could be displayed by the pressure gauge. When altitude difference (Δh) between the two water column showed the maximum, Δp reached the peak. σ could be expressed by the following formula:

$$\sigma = \rho_w g \Delta h_{max} \cdot R/2 \quad (2)$$

where ρ_w was the density of water, and Δh_{max} was the maximum altitude difference between the two water columns in the pressure gauge.

The wetting balance tests were performed with SAT-5100 of Rhesca Co. Surface tension and interfacial tension made the solder 'climb' to the test Cu piece, as shown in Fig. 3. Wetting force (F_W)[15] was defined as the force with which the melt could climb the Cu piece. The piece was suspended from a sensitive balance. It was immersed at a predetermined speed before the end of it reached a controlled depth into the solder melt at a special temperature. The resultant vertical force of buoyancy and wetting force of the Cu piece could be detected by a transducer and recorded. Wettability was determined by the examination of the vertical forces as a function of time. In the present experiments, the Cu piece was immersed at a speed of 20 mm/s, before the immersion depth reached 2 mm. After keeping it for 5 s, the Cu piece was taken out. A middle active rosin flux (RMA) was used in the wetting balance experiments.

3 RESULTS

3.1 Surface tension

Fig. 4(a) shows the surface tensions of Sn-8Zn-3Bi-(0−0.15) Nd solder melts in air at 200−240 ℃. It is clear that the surface tension of the solders decreases with the increase of temperature. Adding minute amount of Nd into the base alloy causes the decrease of the surface tension. With addition of 0.05% Nd, the surface tension reaches the minimum. When additive of Nd rises to

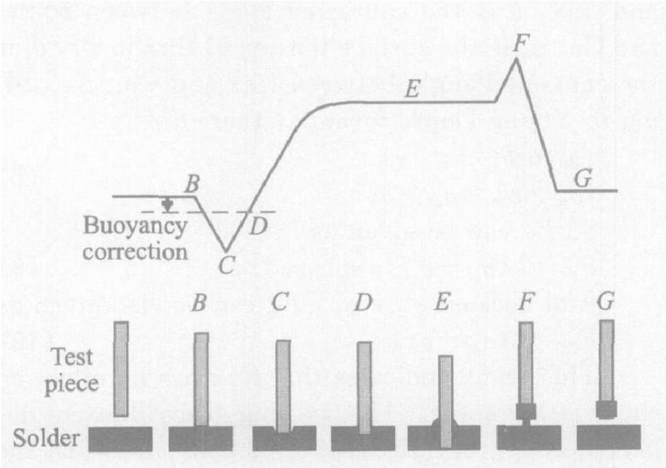

Fig. 3 Schematic diagram of wetting balance measurement

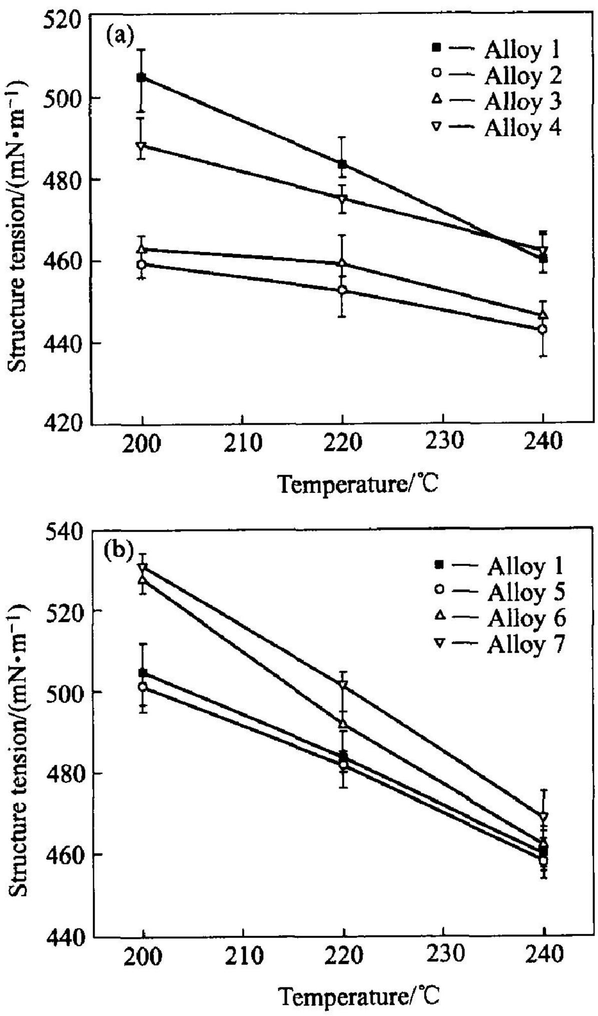

Fig. 4 Surface tension as function of temperature
(a) —Sn-8Zn-3Bi-(0 − 0.15) Nd melts;
(b) —Sn-8Zn-3Bi-(0 − 0.15) La melts

0.15%, the surface tension at 240 ℃ increases beyond that of the base alloy, and the surface tensions at 200 ℃ and 220 ℃ are still lower than that of the base alloy.

As shown in Fig. 4(b), adding minute amount of La can also decrease the surface tension of the solder melts until additive content of La reaches 0.10%. Compared with Fig. 4(a), it is obvious that the effectiveness of La is not as strong as Nd. Moreover, temperature shows a strong effect on the surface tension of La-contained Sn-8Zn-3Bi solders. It indicates that soldering temperature should be raised enough to decrease the surface tension of La-contained Sn-8Zn-3Bi solders, because the wetting performance is based on low surface tension of the solder melts.

3.2 Wetting force and wetting time

Fig. 5(a) shows the wetting balance curves of Sn-8Zn-3Bi-(0 − 0.15) Nd solder melts on Cu substrate. It is obvious that the wetting force of the solders increases with adding minute amount of Nd into the base alloy. The optimal additive content of Nd is 0.10%. The wetting force decreases when Nd content reaches 0.15%. Adding minute amount of La into the base alloy can also improve the wetting force of the solders, and the optimal additive content is also 0.10%. But compared with Nd-contained solders in Fig. 5(b), the effectiveness of La is not as strong as Nd. Moreover, the additive of Nd shortenes the wetting time of the solder melts on Cu substrate.

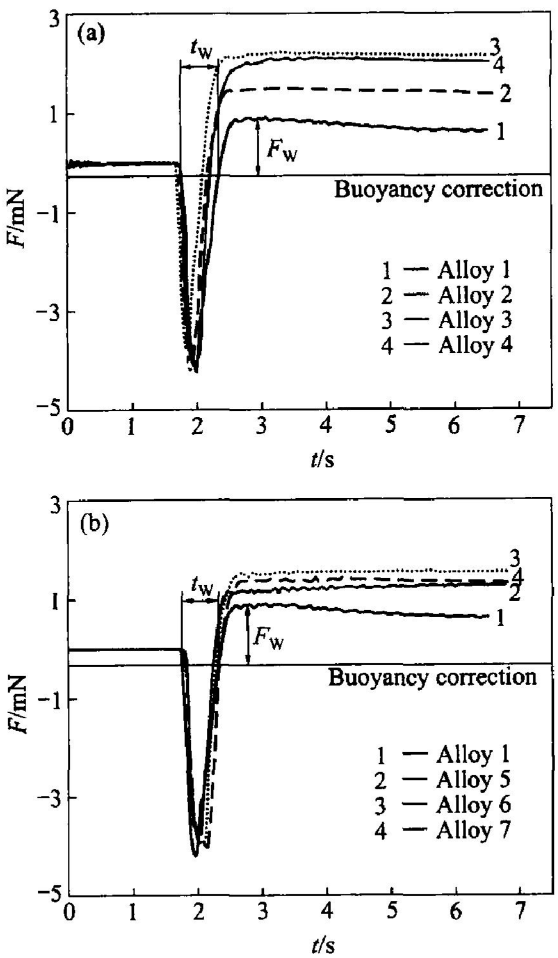

Fig. 5 Wetting balance curves of solders
(a) —Sn-8Zn-3Bi-(0 − 0.15) Nd;
(b) —Sn-8Zn-3Bi-(0 − 0.15) La

4 DISCUSSION

Wetting balance test is a common method to evaluate wetting behavior of solders on substrates. It provides two quantitative parameters, wetting force and wetting time, to denote wetting behavior. Wetting time occurs when the test piece is acted on by buoyancy only and the surface of solder just reaches horizontal, as the point D in Fig. 3. Wetting time depends on wetting kinetics of soldering action, and it reveals wetting speed. The surface tensions of solder and substrate, the interfacial tension between solder and substrate relate to the wetting force, so the wetting force achieved from a wetting balance curve may be used to investigate these tensions.

As shown in Fig. 6, only the buoyancy and the wetting force act on the Cu piece immersed into the solder. The relationship of them is

$$F_W = F + \rho g V \quad (3)$$

where F_W is the wetting force, F is the resultant force acted on the Cu piece (the value in ordinate of wetting balance curves), and $\rho g V$ is the buoyancy.

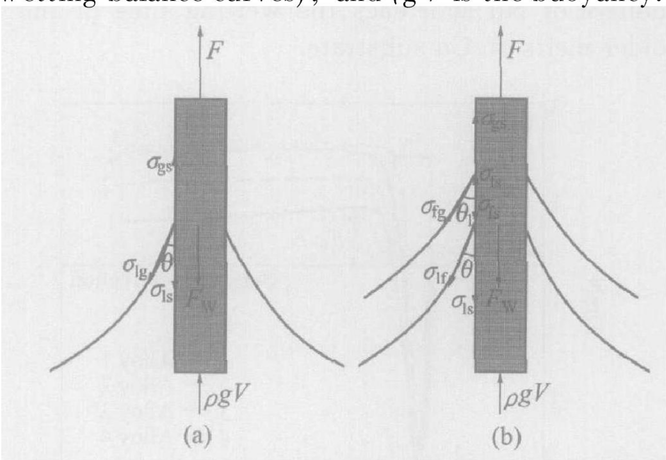

Fig. 6 Schematic diagram of wetting behavior on Cu

As shown in Fig. 6(a), if no flux is applied, F_W can be expressed as

$$F_W = L\sigma_{lg}\cos\theta \quad (4)$$

where L is the perimeter of Cu piece, σ_{lg} is the surface tension of solder in air, and θ is the contacted angle between solder and Cu.

According to Young-Dupre formula, there is

$$\sigma_{lg}\cos\theta = \sigma_{gs} - \sigma_{ls} \quad (5)$$

where σ_{gs} is the surface tension of Cu in air, σ_{ls} is the interfacial tension between solder and Cu.

So F_W can be also expressed as

$$F_W = L(\sigma_{gs} - \sigma_{ls}) \quad (6)$$

As shown in Fig. 6(b), if flux is used, F_W can be expressed as

$$F_W = L\sigma_{lf}\cos\theta + L\sigma_{fg}\cos\theta_1 \quad (7)$$

where σ_{lf} is the interfacial tension between solder and flux, θ is the contacted angle between solder and Cu, σ_{fg} is the surface tension of flux in air, θ_1 is the contacted angle between flux and Cu. According to Young-Dupre formula, there are

$$\begin{cases} \sigma_{lf}\cos\theta = \sigma'_{fs} - \sigma_{ls} \\ \sigma_{fg}\cos\theta_1 = \sigma_{gs} - \sigma_{fs} \end{cases} \quad (8)$$

So F_W can be given as

$$F_W = L(\sigma_{gs} + \sigma'_{fs} - \sigma_{fs} - \sigma_{ls}) \quad (9)$$

And because $\sigma'_{fs} = \sigma_{fs}$, F_W can be also given as

$$F_W = L(\sigma_{gs} - \sigma_{ls}) \quad (10)$$

This result indicates that flux has no effect on the wetting force. The wetting force linearly depends on $\sigma_{gs} - \sigma_{ls}$. Because σ_{gs} is constant when the same Cu pieces are used in the tests, the wetting force only depends on the interfacial tension σ_{ls} between solder and Cu substrate. It reveals that the wetting force increases with the decrease of σ_{ls}.

The wetting forces achieved from the wetting balance curves in this study show that additive of Nd or La improves the wetting force of the Sn-8Zn-3Bi based solders. According to the relationship between the wetting force and σ_{ls}, the increase of the wetting force results from the decrease of σ_{ls}, which demonstrates that additive of Nd of La can decrease the interfacial tension between solder and Cu substrate.

As shown in Fig. 7, the contact angle θ between solder and Cu substrate is a very important parameter which characterizes the wettability of solder. θ can be given by the Young-Dupre formula as follows:

$$\theta = \cos^{-1}(\sigma_{gs} - \sigma_{ls})/\sigma_{lg} \quad (11)$$

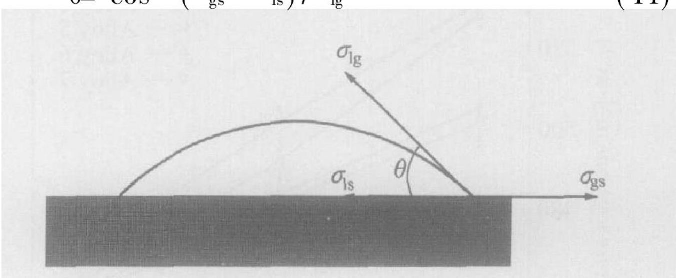

Fig. 7 Schematic diagram of wetting angle

The results in this paper have shown that minute addition of Nd or La decreases σ_{lg} and σ_{ls}. According to the above formula, θ ought to decrease with the decrease of σ_{lg} and σ_{ls}. Therefore, it can be concluded that minute additive of Nd or La can improve the wettability of the Sn-8Zn-3Bi solders.

θ can be calculated by F_W and σ_{lg}. The calculated results for the contact angles are listed in Table 2. The effect of Nd or La on θ of the Sn-8Zn-3Bi solders can be seen from the table. θ of the Sn-8Zn-3Bi-0.1Nd solder is the minimum among all solders in this study, which results from stronger effectiveness of Nd on decreasing the surface tension of solder and the interfacial tension between solder and Cu. The additive of Nd shortens the wetting time of the solder melts on Cu substrate. Therefore, Nd is a stronger effective element than La on improving wettability.

Table 2 Contact angles of solders on Cu substrates

Alloy No	F_W/mN	σ_{lg}/(mN • m^{-1})	θ/(°)
1	1.21	460	74.9
2	1.77	443	66.4
3	2.52	446	55.6
4	2.37	462	59.1
5	1.52	458	71.2
6	1.86	462	66.2
7	1.55	469	70.7

5 CONCLUSIONS

1) Minute amount of Nd or La addition to Sn-8Zn-3Bi solder causes significant decreases of the surface tension of the solder melts at 200 - 240 ℃ and the addition of Nd is more effective on reduction of surface tension than that of La.

2) Nd or La addition has the effect on enhancing the wetting force of the solder melts on Cu substrate, which results from the decrease of interfacial tension between the solder melt and Cu substrates. In the present investigation, the wetting force reaches the maximum when 0.1% of Nd is added to the base alloy.

3) The contact angle between the Sn-8Zn-3Bi base solders and Cu substrate decreases with the addition of Nd or La and the minimum of the contact angle is obtained from the solder with 0.1% of Nd addition.

REFERENCES

[1] Mulugeta A, Guna S. Lead-free solders in microelectronics [J]. Materials Science and Engineering R, 2000, 27(5-6): 95-141.

[2] Katsuki S. Advances in lead-free electronics soldering [J]. Current Opinion in Solid State and Materials Science, 2001, 5(1): 55-64.

[3] Sung K K, Amit K S. Lead(Pb)-free solders for electronic packing [J]. Journal of Electronic Materials, 1994, 23(8): 701-707.

[4] ZHANG Li, XIAN Ai-ping, WANG Zhong-guang, et al. Effect of strain rate on the tensile properties of Sn-9Zn eutectic alloy [J]. Acta Metallurgica Sinica, 2004, 40(11): 1151-1154. (in Chinese)

[5] Shiue R K, Tsay L W, Lin C L, et al. The reliability study of selected Sn-Zn based lead-free solders on Au/Ni-P/Cu substrate [J]. Microelectronic Reliability, 2003, 48(4): 1047-1051.

[6] Katsuki S, Toshikazu M, Hiroji N, et al. Heat resistance of Sn-9Zn/Cu interface with or without coating [J]. Journal of Material Research, 2000, 15(4): 884-891.

[7] Lin K L, Wen L H. The wetting of copper by Al-Zn-Sn solders [J]. Journal of Materials Science: Materials in Electronics, 1998, 9(1): 5-8.

[8] Lin K L, Shih C L. Wetting interaction between Sn-Zn-Ag solders and Cu [J]. Journal of Electronic Materials, 2003, 32(2): 95-100.

[9] YU Da-quan, ZHAO Jie, WANG Lai, et al. Wetting properties of Sn-9Zn solder alloy with trace rare earth elements [J]. The Chinese Journal of Nonferrous Metals, 2003, 31(9): 921-927. (in Chinese)

[10] XIE Hai-ping, YU Da-quan, MA Hai-tao, et al. Microstructure, wettability, mechanical properties of Sn-Zn-Cu lead free solder [J]. The Chinese Journal of Nonferrous Metals, 2004, 14(10): 1694-1699. (in Chinese)

[11] CHEN Guo-hai, LI Xiao-yan, GENG Zhi-ting, et al. The Study on the new type lead-free solder alloys Sn-Zn-Ga [J]. Rare Metal Materials and Engineering, 2004, 33(11): 1222-1225. (in Chinese)

[12] Taguchi, Toshihiko, Katoh, et al. Lead-free Solder Alloys [P]. US 6503338, 2003.

[13] Kim Y S, Kim K S, Hwang C W, et al. Effect of composition and cooling rate on microstructure and tensileproperties of Sn-Zn-Bi alloys [J]. Journal of Alloys and Compounds, 2003, 352(3): 237-245.

[14] Zhou J, Sun Y S, Xue F. Properties of low melting point Sn-Zn-Bi solders [J]. Journal of Alloys and Compounds, 2005, 397(1-2): 260-264.

[15] Wassink R J. Soldering in Electronics [M]. Ayr, Scotland, Electrochemical Publications Limited, 1984.

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