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ELECTRICAL AND MECHANICAL STUDIES OF THE Sn-Ag-Cu-Bi AND Sn-Ag-Cu-Bi-Sb LEAD FREE SOLDERING MATERIALS

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The electrical resistivity and the tensile strength of two near ternary eutectic Sn-Ag-Cu and four solder alloys close to ternary eutectic Sn-Ag-Cu with different Bi content as well as eight Sn- Ag-Cu-Bi with different Sb content in the form of wires were investigated. The four-probe technique was used for electrical parameters measurements. Equipment of the author's own construction for the tensile strength measurement was applied. It was found that the additions of Bi and Sb to Sn-Ag-Cu near eutectic alloys increase the resistivity and the tensile strength and that the resistivity of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys is comparable with those of Pb-Sn solders for the bismuth and antimony content of about 3 atomic percent.

1. Introduction

In a previous work [1] the investigations were conducted for eutectic Sn-Ag and two alloys close to ternary eutectic Sn-Ag-Cu. It has been found that the electrical and the mechanical properties of the investigated alloys are comparable with the literature data for eutectic Sn-Ag and the traditional tin-lead solders. For individual solder joint between the surface mount resistor and PCB, the joint resistance below 0.3 mΩ and the shear strength above 20 MPa were achieved. The electrical resistivity of the solders must be sufficiently low to permit current flow, without heating the joint. On the other hand the mechanical strength of the solders has to be sufficiently high to attach the component to PCB (Printed Circuit Board). It is well known from literature [2] that by addition of Bi to near eutectic Sn-Ag-Cu solders, it is possible to obtain

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solder composition with very good mechanical properties, (see Table 1). By balancing Ag, Cu and Bi contents in the alloy it is also possible to reduce the alloy melting temperature from 217°C to 208°C. Bi plays a major role in the reduction of the alloy melting temperature. However, the amount of Bi that can be added is limited by drastic degradation in fatigue life and plasticity. The composition Sn3.1Ag3.1Bi0.5Cu (mass %) exhibited the best balance of desirable properties, high strength with sufficient plasticity. The crucial role in this phenomena is played by Ag_3Sn and Cu_6Sn_5 particles in the Sn-matrix of Sn-Ag- Bi-Cu system. These particles build a long-range internal stress, resulting in a strengthening effect. They also blocked cracks propagation. In addition, the formation of Ag_3Sn and Cu_6Sn_5 particles can indirectly partition finer Sn — matrix grains. Thus, the resulting overall finer microstructure is expected. The silver content higher than about 3%, certainly increases the volume fraction of Ag_3Sn particles which results in higher strength but lower plasticity and fatigue life.
As an example resistivity and tensile strength from [3], [4] and [2] of similar solders as well as the resistivity of pure metals used for their production are summarized in Table 1.

TABLE 1

Room temperature resistivity or tensile strength for some Sn-Ag-Cu-Bi solders

Materials mass %	Resistivity [μΩcm]	Tensile strength [MPa]	Pure metals	Resistivity [μΩcm]
Sn3.6Ag1.0Cu	12.99@	48.0#	Ag	1.62#
Sn 3.0Ag 0.5Cu 2.2Bi	—	63.0*	Sn	11.5#
Sn3.43Ag0.94Cu1.77Bi	—	79.0*	Bi	115.0#
Sn 2.0Ag 0.5Cu 7.5Bi	—	92.7#	Cu	1.68#
Sn 3.0Ag 3.0Cu 2.0Bi	10.6#	—		

@ from reference [4], # from reference [3], * from reference [2]

The aim of the paper is to investigate how the addition of Bi and Sb to near eutectic Sn-Ag-Cu alloys influence the electrical and mechanical properties of the investigated solders. In the next paper, the experiments will be conducted using the PCB with the jumpers soldered by the lead- free solder alloys.

2. Measurements of the resistivity and the tensile strength

For the resistivity measurement the four-probe method has been used with the application of Keithley 2001 multimeter. The tensile strength was calculated from the measurements of the tensile force with the accuracy of 0.1 N. The resistivity and the tensile force investigations were conducted using a wire with a diameter of 1mm. Before the mechanical and the electrical testing the wire samples were annealed at 100°C for 1 h for structure stabilization. The details of the used measurement techniques can be found in our previous paper [1].

3. Results and discussion

The results for the quaternary and the quinary alloys are presented in the Tables 2 and 3. In the next part of the work they are shown in the form of graphs (Figs 1-12).

TABLE 2

Resistivity ρ and tensile strength R_m of lead-free solder quaternary Sn-Ag-Cu-Bi alloys (mean value ± standard deviation)

Sn-Ag-Cu-Bi Alloys Composition in atomic %	ρ [$\mu\Omega \cdot m$]	R_m [$N \cdot mm^{-2}$]
@$(Sn\text{-}Ag)_{eut}$	0.118±0.003	41.6±5.5
@Sn2.76Ag0.46Cu	0.117±0.005	40.2±4.0
@Sn3.13Ag0.74Cu	0.122±0.005	68.5±4.9
Sn3.13Ag0.48Cu4.02Bi	0.148±0.003	92.7±3.4
Sn2.95Cu0.53Cu6.81Bi	0.158±0.003	113.6±4.5
Sn2.75Ag0.86Cu3.86Bi	0.149±0.004	119.8±2.7
Sn2.86Ag1.01Cu6.62Bi	0.164±0.006	154.4±9.0

@ — data from our previous work [2004Kis]

TABLE 3

Resistivity ρ and tensile strength R_m of lead-free solder quaternary Sn-Ag-Cu-Bi-Sb alloys (mean value ± standard deviation)

Sn-Ag-Cu-Bi-Sb Alloys Composition in atomic %	ρ	R_m
	[$\mu\Omega m$]	[N/mm^2]
Sn3.55Ag0.5Cu3Bi3Sb	0.166±0.001	157±30
Sn3.48Ag0.5Cu3Bi5SB	0.191±0.001	147±31
Sn3.48Ag0.5Cu5Bi3Sb	0.176±0.001	133±14
Sn3.40Ag0.5Cu5Bi5Sb	0.189±0.001	152±25
Sn3.53Ag1Cu3Bi3Sb	0.169±0.001	141±16
Sn3.46Ag1Cu3Bi5Sb	0.182±0.001	168±23
Sn3.46Ag1Cu5Bi3Sb	0.178±0.001	166±23
Sn3.38Ag1Cu5Bi5Sb	0.187±0.001	177±13

4. Physical and electrical properties of the quaternary Sn-Ag-Cu-Bi and quinary Sn- Ag-Cu-Bi-Sb lead-free solder alloys in the wire form

The room-temperature resistivity measurements of solders in the wire form are presented in Table 2 and in Fig. 1. Each value represents the average of 50 measurements. The resistivity of the eutectic Sn3.5Ag wire was measured as 11.81μΩcm, in good agreement with the published value of 12.30 μΩcm [4]. The electrical resistivity of the near- eutectic Sn-Ag-Cu solders is very close to that of the eutectic Sn-Ag alloy. With increasing Bi content, the resistivity increased, as shown in Figure 1. There is no difference in resistivity increase for solders with 0.47% Cu and with 0.80-1.01% Cu. The increase of solders resistivity with increase Bi contents in alloy was expected, because the Bi resistivity is significantly higher than that of other additives.

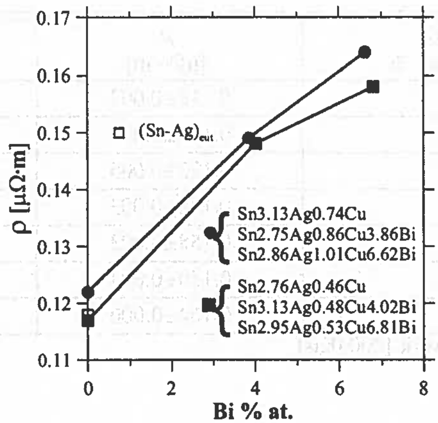

Fig. 1. Effect of the bismuth on the resistivity of Sn2.76Ag0.46Cu and Sn3.13Ag0.74Cu solder alloys

Nevertheless, the resistivity of the investigated solder is comparable with the resistivity of Sn-Pb solder (14.44 μΩcm [3]), and is sufficient for functioning of electrical circuits. The resistivity measurements of the quinary Sn-Ag-Cu-Bi-Sb lead-free solder alloys are presented in Table 3 and in Figs 2 and 3. When analyzing the results, it is seen that both Bi and Sb increase the resistivity in comparison to both binary $(Sn\text{-}Ag)_{eut}$ and ternary Sn-Ag- Cu alloys. The increase of the resistivity when Bi or Sb is added to Sn-Ag-Cu

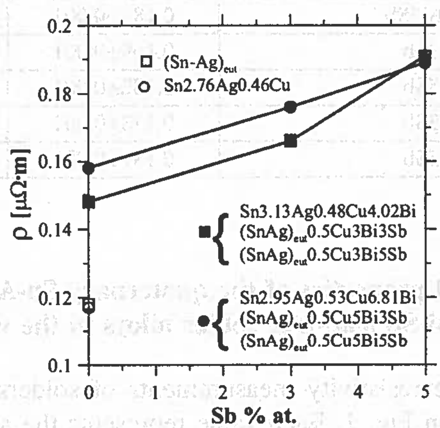

Fig. 2. Effect of the bismuth and antimony on the resistivity of Sn2.76Ag0.46Cu solder alloys

alloys is similar for similar additions these metals. Generally, the quaternary and the quinary alloys are characterized by higher resistivity than binary $(Sn\text{-}Ag)_{eut}$ and the ternary Sn-Ag-Cu lead-free alloys. For alloys with 3% atomic Bi and Sb the resistivity is comparable with those for Pb-Sn solders (14.44 μΩcm, [3]) and is sufficient for good functioning of electric circuits.

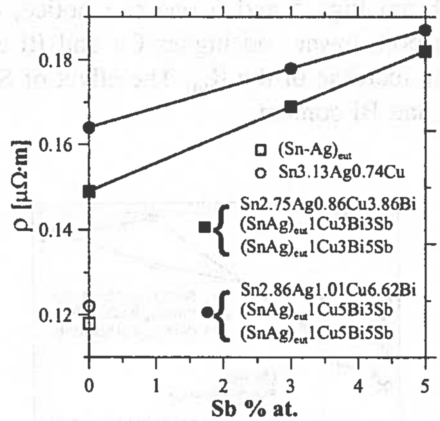

Fig. 3. Effect of bismuth and antimony on the resistivity of Sn3.13Ag0.74Cu solder alloys

The results of tensile strength examination of the investigated alloys in the wire form are shown in Tables 2 and 3 and Figs 4-6. Each data point represents the average value for five to six samples. The measured values of the tensile strength for the quaternary Sn-Ag-Cu-Bi alloys are shown in Fig. 4. and, as it is seen, they are higher than the data cited by H w a n g [2], where the value 63MPa was recorded for the alloy Sn3.0Ag0.5Cu2.2Bi and almost 79 MPa for the alloy Sn3.43Ag0.94Cu1.77Bi and similar to [3] for the alloy Sn2.26Ag0.96Cu4.37Bi. Such difference may be connected

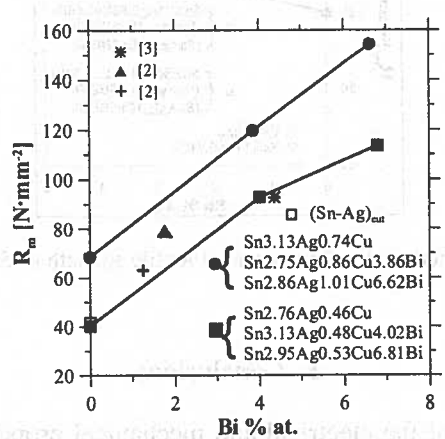

Fig. 4. Influence of bismuth on the tensile strength of Sn.3.13Ag0.7Cu alloys

with the cooling rate after melting which significantly change the grain size and consequently the alloy strength and plasticity.
The influence of the Bi and Sb on the tensile strength of Sn-Ag-Cu alloys is presented graphically in Figs 4-6. It can be noticed that the addition of the Bi to Ag-Sn-Cu increases remarkably the tensile strength of the lead-free Sn-Ag-Cu alloys (see Fig. 4). A similar conclusion can be drawn from the analysis of the effect of Sb additions to Sn-Ag-Cu-Bi alloys. From Figs 5 and 6 one can notice, too, that the quaternary Sn-Ag-Cu-Bi alloys with both lower and higher Cu and Bi concentrations, modified by the antimony, show the increase of the R_m. The effect of Sb addition is greater for the alloys with lower Cu and Bi content.

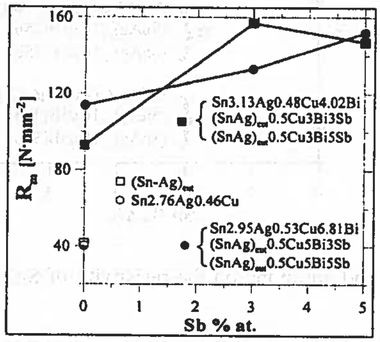

Fig. 5. Influence of bismuth and antimony on the tensile strength of Sn2.76Ag0.46Cu alloys

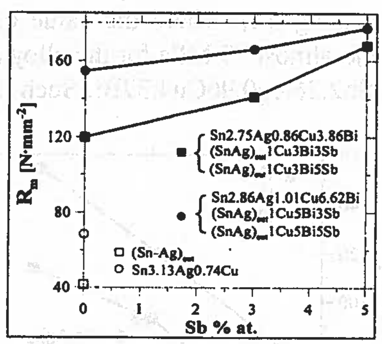

Fig. 6. Influence of bismuth and antimony on the tensile strength of Sn3.13Ag0.74Cu alloys

5. Conclusions

The reported study of the electrical and mechanical properties of the investigated alloys has shown results comparable with the data from literature.

Additions of Bi to near eutectic Sn-Ag-Cu solders increase the solder resistivity from 0.12 μΩm up to 0.16 μΩm. The obtained resistivities of Sn-Ag-Cu-Bi solders are comparable with those of Sn-Pn solders (0.14 μΩm). Addition of Sb to Sn-Ag-Cu-Bi solders increases the resistivity up to 0.18-0.19 μΩm. The resistivities of Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb are higher than that for Sn-Ag-Cu, but from the practical point of view such resistivity changes are not an obstacle to apply solders as the electrical connection materials.

The performed investigations show that by adding Bi to Sn-Ag-Cu solders it is possible to increase significantly the tensile strength of Sn-Ag-Cu-Bi solders. The tensile strength increase of Sn-Ag-Cu-Bi solders with addition of Sb is also observed; nevertheless the increase of the tensile strength with Sb addition is smaller than by the addition of Bi to Sn-Ag-Cu solders. The decrease of plasticity of Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb with the increase the Bi or Sb contents was observed in the alloys. It can be confirmed by the signifivantly higher standard deviation of the tensile strength of Sn-Ag-Cu-Bi-Sb solders than that of Sn-Ag-C-Bi.

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