SnAgCuBi and SnAgCuBiSb solder joint properties investigations

This study investigates the technological properties of quaternary or quinary alloys made by addition Bi or Bi and Sb elements to the SnAgCu solders. The influence of added elements on the electrical and mechanical properties of solder joints created by these solders between PCB and electronic components were evaluated. In "(Sn-Ag)eut+Cu Soldering Materials, Part II: Electrical and Mechanical Studies"[1], the same parameters were investigated for eutectic Sn-Ag and two alloys close to ternary eutectic SnAgCu. It was found that electrical and mechanical properties of the investigated alloys are comparable to the data from literature for eutectic Sn-Ag and the traditional tin-lead solders. For individual solder joint between surface mount chip resistor and PCB the joint resistance below 0.3 mΩ and shear force above 85 N were achieved.

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Keywords: SnAgCuBi, SnAgCuBiSb, Solder Joints, Solder Joint Resistance, Mechanical Properties

Introduction

The most important advantage of SnAgCuBi over SnAgCu solders is the lower melting temperature. In SnAgCuBi, Bi plays a major role in reducing the alloy melting temperature. By balancing Bi as well as Ag and Cu contents in the alloy, it is possible to reduce the alloy melting temperature from 217°C to 208°C-212°C. However, the amount of Bi that can be added is limited by drastic degradation in fatigue life and plasticity. Too much Bi leads to the presence of a small DSC peak near 138°C, corresponding to the binary SnBi eutectic at 138°C or ternary SnAgBi eutectic at 136.5°C. The presence of such DSC peaks in SnAgCu solders with high Bi contents means that in the alloy there are microstructure regions having low melting eutectics. Such phenomena do not occur if Bi contents in SnAgCuBi alloys are lower than 5 mass %.[2]

The Bi element plays a major role not only for reduction in the alloy melting temperature but also in reduction of surface tension of SnAgCuBi alloys. The surface tension of pure Sn is 557.7 mN/m at 270°C and that of Bi is 378.8 mN/m at 310°C.[3]. The pure Bi surface tension lower than pure Sn means that increasing Bi content in SnBi solders decreases their surface tension. It can be expected that the same effect will occur in SnAgCuBi solders. Such changes of solder surface tension improve solder wettability.

The addition of Bi to SnAgCu alloys increases the mechanical properties of solders. The Bi precipitation-strengthening mechanism generally follows Mott and Nabarro's strain field theory because the alloy strength measured is proportionately related to the volume fraction of Bi precipitates.[4] This suggests that the Bi precipitation-strengthening effect predominantly results from the long-range internal stress built by Bi precipitations. It is expected that Cu at 0.5 wt.% in SnAgCuBi system containing [3] to 3.4 mass % Ag and 3 to 3.1 mass % Bi most efficiently generates the proper amount of Cu_6Sn_5 particles with the finest microstructure size, thus delivering high fatigue life, strength and plasticity.

The addition of Sb to SnAg solder increases the melting temperature[5], but the Cu content beyond 0.5 mass % reduces this disadvantagous effect. The addition of greater than 0.5 mass % Sb or 0.1 mass % Bi is effective in eliminating tin pest phenomena in high Sn content alloys. Tin pest is caused by the transformation of b-Sn to a-Sn when the temperature falls below 13°C. It is results in a large increase in volume, which can induce cracking in the Sn structure.[6] The Sb addition also has the effect of imparting strength and hardness to the Sn25Ag10Sb alloy. The relatively high melting temperature (230-235°C) makes it suitable for high temperature applications. Such alloys were used by Motorola as replacements for SnSi die attach material. The larger amount of Sb may also be responsible for the very poor wetting behavior of SnAgCu alloy. An improper Sb amount can quickly reduce wetting ability.

The aim of the paper is to know how Bi content, higher than 3 mass %, added to near eutectic Sn-Ag-Cu alloys of Cu content 0.26 to 0.40 mass % (0.46-0,74 at.%), influence the exploitation properties of solder joints. Two ranges of Bi content in SnAgCuBi were investigated, the range 6.65-6.91 mass % (3.86 - 4.02 % at.) and the range with significantly higher of Bi content: 11.17-11.45 mass % (6.62 -6.81% at.). In the paper devoted to wettability testing of SnAgCu alloys with Bi content, it was found that the surface tension and interface tension decrease with addition of Bi to ternary SnAgCu alloys in temperature above 200°C.[7] It is expected that with Bi content in SnAgCu, wettability can be more equivalent to SnPb eutectic, which offers better solder joint properties.

The second aim of the investigation is to know how the addition of Bi and Sb elements to SnAgCu with Cu contents 0.26 to 0.53 mass % influences solder joint properties. Two ranges of Bi contents in SnAgCuBiSb were investigated, 5.19 to 8.54 mass % (3 at. % or 5 at. %), as well as two ranges of Sb: 2.98 to 3.03 mass % (near 3 at. %)

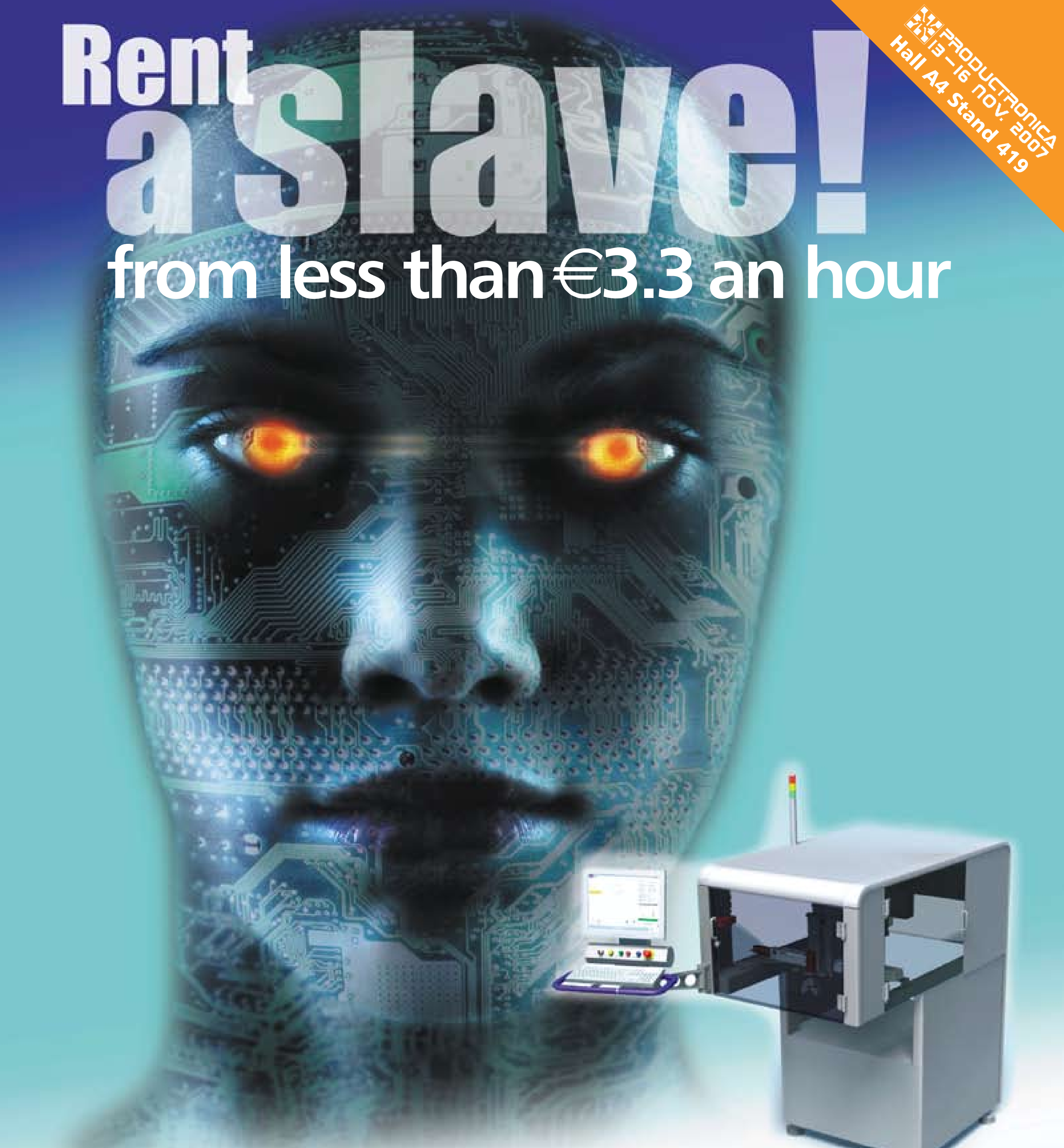

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Table 1. Compositions of quaternary and quinary alloys

Composition of alloy mass %	Composition of alloy atomic %
Sn2.77Ag0.25Cu6.91Bi	Sn3.13Ag0.48Cu4.02Bi
Sn2.56Ag0.27Cu11.45Bi	Sn2.95Ag0.53Cu6.81Bi
Sn2.4Ag0.45Cu6.65Bi	Sn2.7Ag0.86Cu3.86Bi
Sn2.49Ag0.52Cu11.17Bi	Sn2.86Ag1.01Cu6.62Bi
Sn3.17Ag0.26Cu5.19Bi3.02Sb	Sn3.55Ag0.5Cu3Bi3Sb
Sn3.10Ag0.26Cu5.19Bi5.04Sb	Sn3.48Ag0.5Cu3Bi5Sb
Sn3.03Ag0.26Cu8.52Bi2.98Sb	Sn3.48Ag0.5Cu5Bi3Sb
Sn2.99Ag0.26Cu8.52Bi4.96Sb	Sn3.40Ag0.5Cu5Bi5Sb
Sn3.16Ag0.53Cu5.20Bi3.03Sb	Sn3.53Ag1Cu3Bi3Sb
Sn3.09Ag0.53Cu5.20Bi5.00Sb	Sn3.46Ag1Cu3Bi5Sb
Sn3.05Ag0.52Cu8.54Bi2.99Sb	Sn3.46Ag1Cu5Bi3Sb
Sn2.98Ag0.52Cu8.54Bi4.97Sb	Sn3.38Ag1Cu5Bi5Sb

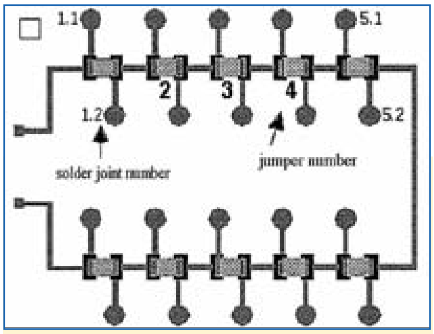

Figure1. The configuration of chip resistors 1206 on PCB for electrical and mechanical measurement.

and significantly higher Sb contents 4.97 to 5.0 mass % (near 5 at. %). The previous wettability results of SnAgCu alloys with Bi and Sb content were shown that the surface tension and interface tension decrease with addition of Sb to SnAgCuBi alloys.8 It is expected that Sb can increase mechanical strength of solder joints.

An experiment based on Taguchi orthogonal arrays L_4 (2^3) for Bi addition and L_8 (2^7) for both Bi and Sb addition was designed, and the results were analyzed by analysis of variance (ANOVA).

Solders for investigation

The composition of quaternary SnAgCuBi

and quinary SnAgCuBiSb solders investigated are presented in *Table 1*.

The solder joints were formed between the terminations of chip resistors (jumpers) and PCB conductors by wave soldering.[1] The jumper terminations and PCB conductors have Sn finish (1.2 µm thick). ROL1 type (3% solid) low activity rosin flux was applied just before soldering. The wave soldering peak temperature was 250°C; soldering time was 2 seconds. The soldering processes were performed by rotary dip method in a laboratory scale using a 2 kg bath of each solder.

Special attention was given to guarantee the same soldering condition for all joint preparation. During soldering, molten solder reacts with conductors on the substrate and component terminations. The Sn layers from the PCB and component termination finishes are dissolved in solder. The interfacial reactions that occur in solder joints can influence the microstructure as well as electrical and mechanical properties of the solder joint.

Resistance of solder joint measurement

The idea of individual joint resistance measurement is based on the four-probe measurement method and was previously described in details in the paper "Resistivity of Lead-free Solder Joints".[8] Keithley 2001 multimeter, option four wire Ohms, was used for such measurements. Automated data acquisition was possible through the use of an own elaborated software program. The idea of solder joint resistance measurement was presented in *Figure 1*. By measuring the current flow through the chain of solder joints and voltage drop on a single solder joint it is possible to calculate the individual joint resistance.

Shear strength of solder joint measurement

Mechanical properties of the solder joints were evaluated by recording the shear force of 1206 jumpers from PCB. The shear force was applied directly to the middle of longer jumper side, parallel to PCB. The value of the shear force consists of three components: solder joints on both jumper sides and adhesive bonding between jumper and PCB.

The influence of Cu and Bi content on the electrical & mechanical properties of the solder joints made by SnAgCuBi alloys

In order to identify how Cu and Bi content in quaternary SnAgCuBi solders influence solder joint resistance and mechanical properties, and experiment based on Taguchi orthogonal arrays was applied in our work. In a performed series of experiments, four SnAgCuBi solder composition with different Cu and Bi contents were prepared. The levels of Cu and Bi contents in SnAgCuBi alloys are called factors. The level of factor A, Cu content, the same as in previous experiments[9], was ~0.5 at%, signed as A1, and Cu ~1.0 at % signed as A2. The Bi levels in SnAgCuBi alloys was ~3 at % signed as B1, and ~5 at. % signed as B2. Above mentioned factors as well as Cu and Bi interaction were assigned to the columns of orthogonal array $L_4(2^3)$, *Table 1*. The solder alloys were manufactured according to the design compositions, and the obtained compositions are shown in the *Table 1*. Next, solder joints were formed between the terminations of jumpers and the PCB's conductors. The individual solder joint resistance and shear force of the jumper were measured. Individual solder joint resistance R_j represents an average value of 100 measurements. The shearing force F_s (for 1206) represents an average value from twenty samples. In the last columns of the υthe average values of measurements for joint resistance and shear force are given.

The results of experiments were analyzed by analysis of variance (ANOVA). To do such analysis, the sum of squares for each factor was calculated:

Equation 1

$$SS_x = X_1^2/n_{x1} + X_2^2/n_{x2} - T^2/N$$

where $X_{1,2}$ is the sum of observations under $X_{1,2}$ levels, $n_{x1,2}$ is the number of observations under $X_{1,2}$ level, T is the sum of all observations and N is the total number of observations. The total sum of squares for all factors is:

Equation 2

$$SS_T = y_1^2 + ..y_i^2 +..y_N^2 - T^2/N$$

where yi is the value of i-th test. To establish which factors have a significant effect on the final result, the variance V_x was estimated for each factor of vx degree of freedom:

Equation 3

$$V_x = SS_x / v_x$$

and F-tests were performed. The F-test is used to test the statistical significance of a factor variance when compared to error variance V_e:

Equation 4

$$F = V_x / V_e$$

The factors, which are significant at 99%, 95% and 90% confidence level, are marked by three, two and one asterisk respectively. The portion of the total variation observed in an experiment attributed to each significant factor is reflected in percent contribution:

Equation 5

$$P\ \% = [(SS_x - v_x\ V_e)/SST] * 100\ \%$$

All factors that were not significant were incorporated into the pooled error epooled. The full ANOVA results of calculations for joint resistance are given in *Table 3* and for shear strength of 1206 jumper in the *Table 4*.

The ANOVA analysis shown in the tables permitted us to estimate the influence of factor levels and interactions between them on solder joint properties. It is possible to calculate the percentage contribution of each factor on solder joint properties. Such calculations are connected with errors according to the (1) – (5) quotations. If the percent contribution due to error is less than 15 % it means that experiment was designed properly. If the percent contribution due to error is high, 50% or more, than some important factors were definitely omitted, conditions were not precisely controlled, or measurement error was extensive. As the results of analysis of variance (ANOVA) it was established that Cu content in alloys is predominantly significant factor (71.88% contribution in variability) which influences the solder joints resistance. Increasing Cu content from 0.46 at. % to 0.74 at. % significantly reduce solder joint resistance, see *Figure 2*.

The influence of increasing Bi content on joint resistance of SnAgCuBi solder alloys is significantly less than Cu, see *Table 3* and *Figure 2*.

Increasing Bi concentration decreases solder joint resistance. Such results were not expected. In previous investigation9 was shown that the solder resistivity increases with increasing of Bi element addition. The differences can be explained

Table 2. The quaternary alloys assigned to $L_4(2^3)$ orthogonal array and R_j, F_s results

Test No	Factors			Composition of alloy	Results R_j	F_s (for 1206)
	A	B	AxB	mass %	[mW]	[N]
1	1	1	1	Sn2.77Ag0.25Cu6.91Bi	0.268	105.8
2	1	2	2	Sn2.56Cu0.27Cu11.41Bi	0.223	92.2
3	2	1	2	Sn2.40Ag0.45Cu6.65Bi	0.188	92.6
4	2	2	1	Sn2.49Ag0.52Cu11.17Bi	0.179	87.3

Table 3. ANOVA for average values of Rj

Factor	SS	v	V	F	SS'	P%
Cu	0.0038	1	0.0038	11.8642**	0.0035	71.8807
Bi	0.0007	1	0.0007	2.2500	0.0004	8.2704
CuxBi	0.0003	1	0.0003	1.0000	0.0000	-
T	0.0049	3	----	----	0.0049	100.0000
Error	0.0003	1	0.0003	----	0.0010	19.8489

Table 4. ANOVA for average values of Fs (for 1206)

Factor	SS	v	V	F	SS'	P%
Cu	79.21	1	79.21	4.2839	60.72	32.97
Bi	86.49	1	86.49	4.6777	68.00	36.92
CuxBi	18.49	1	18.49	1.0000	55.47	30.12
T	184.19	3	----	----	184.19	100.00
e	18.49	1	18.49	----	0	0

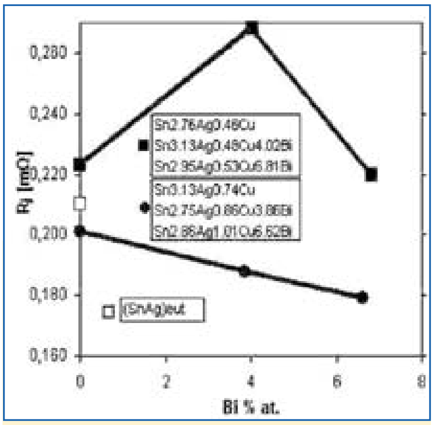

Figure 2. Effect of the bismuth content in SnAgCuBi solders on the solder joint resistance.

if *Equation* 6 is more precisely analysed.

Equation 6

$$R = \rho * l/S$$

Where: ρ - solder resistivity, l - joint length, S - solder cross-section.

Three factors may influence solder joint resistance, solder resistivity ρ, joint length "l" and area of solder cross-section "S". Joint length "l" is constant and is defined by the distance between laminate and

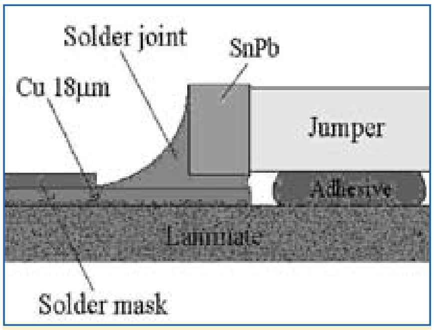

Figure 3. The shape of solder joint.

jumper contact and practically is defined by adhesive thickness, *Figure 3*. Solder resistivity depends on solder composition and increases with Bi contents. The area of solder cross section "S" depends on solder wettability: better wettability means a smaller cross section because the solder meniscus is more concave, see *Figure 3*. The decreasing solder cross section is the dominate factor, and solder joint resistance decreases with Bi addition to solders.

Mechanical properties of the solder joints were evaluated by recording the shear force of 1206 jumpers from PCB. The results of the examination of the joint shear strength at room temperature are shown in *Table 2*. Each data point represents an average value from twenty samples. The results of ANOVA analysis related to

shear force measurements show that both elements, Cu and Bi, and their interaction influence the shear force at the same level, but there are not significant factors.

The formation of intermetallic compounds Cu_6Sn_5 and Ag_3Sn may be responsible for the mechanical properties of solder joints (in our case shear force), see *Figure 4*. Increase the Bi contents above 4 at. % caused decrease mechanical properties (shearing force). The alloys with ~ 1.0 at. % Cu has slightly worse mechanical properties than alloys with ~ 0.5 at. % Cu. The reference measurements with SnPb solder joints manufactured in the same conditions gave the average shearing force in the range of 100 N. Obtained shear force ranges for solder joints manufactured by SnAgCuBi solders are acceptable from practical point of view.

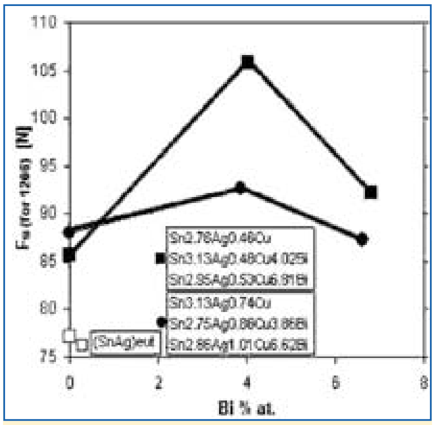

Figure 4. Effect of the bismuth content in SnAgCuBi solders on the solder joint shear force.

The influence of Cu, Bi and Sb content on the electrical & mechanical properties of the solder joints made by SnAgCuBiSb alloys

In order to identify how Cu, Bi and Sb content in quinary SnAgCuBiSb solders influence the solder joint resistance and mechanical properties the orthogonal array $L_8(2^7)$ was designed. The level of factor A, Cu content was the same as in the above experiments for quaternary alloys: ~0.5 at. % of Cu was signed as A1, and ~1.0 at. % of Cu signed as A2. The Bi levels in SnAgCuBiSb alloys were signed as B1 (~3 at. % of Bi) and B2 (~5 at. % of Bi). The Sb levels in SnAgCuBiSb alloys was signed as C1 (~3 at. % of Sb) and C2 (~5 at. % of Sb). Above mentioned factors were assigned to the columns of orthogonal array $L_8(2^7)$ *Table 5*. The A & B, A & C and B & C interactions were also predicted and assigned to columns of orthogonal array.

Table 5. The quinary alloys assigned to L_8 (2^7) orthogonal array and R_j, F_s results

Test No	Factors							Composition of alloy	Results	
	A Cu	B Bi	AxB CuxBi	C Sb	AxC CuxSb	BxC BixSb	D	mass %	R_j [mΩ]	F_s (for 1206) [N]
1	1	1	1	1	1	1	1	SnAg0.26Cu5.19Bi3.02Sb	0.244	122.3
2	1	1	1	2	2	2	2	SnAg0.26Cu5.19Bi5.04Sb	0.246	113.7
3	1	2	2	1	1	2	2	SnAg0.26Cu8.52Bi2.98Sb	0.235	99.5
4	1	2	2	2	2	1	1	SnAg0.26Cu8.52Bi4.96Sb	0.249	91.9
5	2	1	2	1	2	1	2	SnAg0.53Cu5.20Bi3.03Sb	0.237	81.7
6	2	1	2	2	1	2	1	SnAg0.53Cu5.20Bi5.00Sb	0.246	79.4
7	2	2	1	1	2	2	1	SnAg0.52Cu8.54Bi2.99Sb	0.233	94.6
8	2	2	1	2	1	1	2	SnAg0.52Cu8.54Bi4.97Sb	0.242	93.8

Table 6. ANOVA for average values of Rj

Factor	SSx	v	V	F	SS'	P%
Cu	0,000032	1	0,000032	2,053	0,0000164	-
Bi	0,000025	1	0,000025	1,572	0,0000089	-
CuxBi	0,000000	1	0,000000	0,032	-0,0000151	-
Sb	0,000145	1	0,000145	9,273**	0,0001289	54,167
CuxSb	0,000000	1	0,000000	0,032	-0,0000151	-
BixSb	0,000018	1	0,000018	1,155	0,0000024	-
D	0,000018	1	0,000018	1,155	0,0000024	-
T	0,000238	7	----	----	0,0002380	100,000
e	0,000093	6	0,000016	----	0,0001091	45,833

Table 7. ANOVA for average values of Fs

Factor	SSx	v	V	F	SS'	P%
Cu	758,551250	1	758,551250	35,701***	737,30	48,796
Bi	37,411250	1	37,411250	1,761	16,16	-
CuxBi	646,201250	1	646,201250	30,413***	624,95	41,361
Sb	46,561250	1	46,561250	2,191	25,31	-
CuxSb	21,451250	1	21,451250	1,010	0,20	-
BixSb	0,781250	1	0,781250	0,037	-20,47	-
D	0,031250	1	0,031250	0,001	-21,22	-
T	1510,988750	7	----	----	1510,99	100,000
e	106,236250	5	21,247250	----	148,73	9,843

In a series of experiments, eight solder compositions were prepared with different Cu, Bi and Sb contents. Next, the solder joints were formed between the terminations of the jumpers and the PCB's conductors. The individual solder joint resistance and shear force of jumper were measured. Individual solder joint resistance Rj represents an average value of 100 measurements. The shearing force Fs (for 1206) represents an average value from twenty samples. In the last columns of *Table 5*, the average values of measurements for joint resistance and shear force are given.

The change of joint resistances is not significant and practically not influences on solder joint exploitation parameters. The shear force for investigated alloys is in the range from 80 N up to 120 N. The reference measurements with SnPb solder joints manufactured in the same conditions gave the average shearing force in the range of 100 N.

The ANOVA analysis and F-test were used to find the relation between solder composition and measured parameters of quotations (1) - (5). The results of such analysis were presented in *Tables 6 and 7*.

The analysis showed that the biggest influence on solder joint properties have Cu and Sb concentration in the alloy as well as interaction between Cu and Bi. Increasing Sb concentration caused an increase in solder joint resistances (*Figure 5*).

The ANOVA analysis showed that biggest influence on solder joint resistance was the Sb element. Increasing Sb concentration caused increase the solder joint resistance (*Figure 5*).

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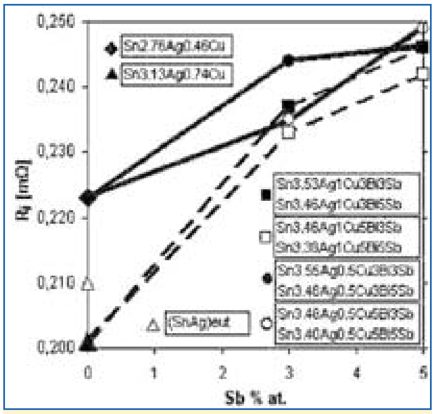

Figure 5. Effect of the Sb content in SnAgCuBiSb solders on the solder joint resistance.

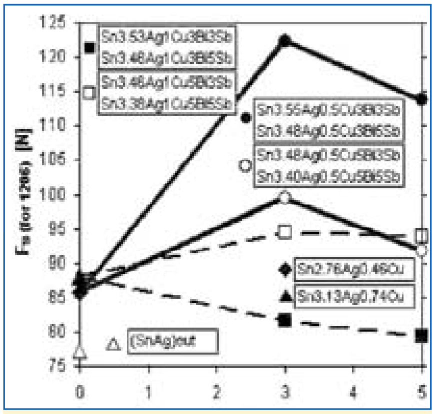

Figure 6. Effect of the Sb content in SnAgCuBiSb solders on the solder joint shear force.

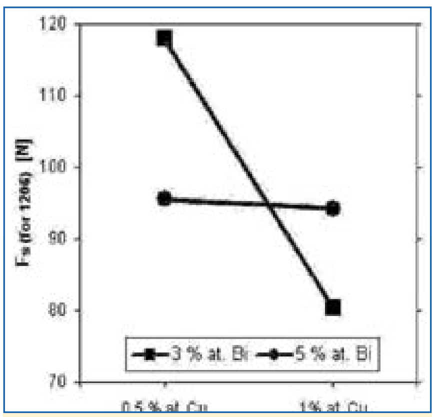

Figure 7. The influence of Cu and Bi content on shear force of SnAgCuBiSb solders: Cu & Bi interaction.

The solder joint shear strength of SnAgCuBiSb solders increases to some amount of Sb element (in our case up to 3 at. %) further increasing of Sb content decreases the shear force, *Figure* 6.

Besides that, the shear force of solder joints is influenced by change of Cu concentration in alloy as well as by interaction of Cu and Bi elements, *Figure 7*.

The shear force of solder joints is independent of Cu concentration in SnAgCuBiSb solders for higher Bi content, but for lower Bi contents the solder joint shear strength strongly depends on Cu concentration in quinary alloys; it decreases with increasing Cu content.

Table 8. Electrical and mechanical parameters of solder joints made by chosen SnAgCuBi alloy

Composition of alloy mass %	Rj [mW]	Fs (for 1206) [N]
Sn2.76Ag0.27Cu7.44Bi	0.261	85.7

Confirmation experiment

To compare the results obtained for the technological properties of solder joints manufactured by quaternary and quinary alloys, it was observed that quaternary SnAgCuBi alloys are better for application than quinary SnAgCuBiSb alloys. Performed experiments showed that the best technological and exploitation properties were achieved for SnAgCuBi solder with ~0.5 at. % Cu and ~4 at. % Bi. Such alloy offers high shear force with acceptable low solder joint resistance. To confirm the obtained results, a confirmation experiment was done. The SnAgCuBi solder was manufactured again with ~0.5 at. % Cu and ~4 at. % Bi. The components and technological parameters of new fabricated solder were measured again; the results of investigation are presented in *Table* 8.

The experiment confirmed that the new manufactured SnAgCuBi solder has similar properties to the previous manufacture solder and the technological and exploitation parameters are fully repeatable and acceptable.

Conclusions

The reported study of the electrical and mechanical properties of the investigated SnAgCuBi solder joints have shown the advantageous changes compare to the SnAgCu solders. The tendency of changes after Bi element addition is comparable to the data from literature.

The solder joint resistances formed between 1206 jumpers and PCBs are in the range 0.18-0.25 mΩ. Joint resistances for SnAgCuBi solders are slightly higher than for SnAgCu solders. The solder joint resistance changes are resulted not only from higher solder resistivity but also from the better wettability of solders with higher Bi contents.

The shear force of solder joints formed by wave soldering with investigated SnAgCuBi solders was in the range of 85-106 N. Such high values are high enough from a practical point of view and comparable to solder joints formed with SnPb solders.

The reported study of the electrical and mechanical properties of the investigated SnAgCuBiSb solder joints have shown rather the disadvantageous changes compare to the SnAgCuBi and SnAgCu solders. The tendency of changes after Sb element addition is not comparable to the all data from literature. Increasing Sb concentration in SnAgCuBiSb alloys caused increase the solder joint resistance. The solder joint shear strength increases with Sb element, but only to the 3 at. % than increasing of Sb content decreases the shear force. Besides that, the shear force of solder joints is influenced by the change of Cu concentration in alloy as well as by interaction of Cu and Bi elements.

The confirmation experiment has shown that the SnAgCuBi solder has similar properties to the previous manufacture solder and the exploitation parameters are fully repeatable and acceptable.

To compare with near eutectic SnAgCu solders with investigated SnAgCuBi and SnAgCuBiSb alloys, it should be stated that SnAgCuBi solder (Sn2.76Ag0.27Cu7.44Bi mass %) exhibits better properties from a technological point of view and can be used for soldering processes.

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Q10. What challenges and opportunities face the electronics manufacturing industry in the years ahead?

Competition will require manufacturers to push their production costs even lower. Placing ever smaller components more quickly, accurately and economically will also play an increasingly important role.

To accomplish all this, electronics manufacturers and equipment makers will have to work together even more closely and individually. We already see this with our service concepts. Customers will need a lot more process consulting from us in the future. The successful vendors will be those who are able to offer highly productive system solutions consisting of hardware, software, consulting and services.

Thank you very much for this interview, Mr. Lauber