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Above specify characteristics of ecological soldering alloy

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Abstract – The quality of soldering connexions from electronic devices is determined by various types of factors, most important are the materials used for soldering, soldering technology, soldering process parameters, electronic components type and the plate for components placement. Between those factors is a strong connection, the interaction between these factors is critical, specially for automatizated soldering process.

I. INTRODUCTION

Taking into account that for an application we have only the components and plates, as a result the only factors that can be modify are soldering materials and in some cases soldering technology.

From here, as a result the importance of optimal selection for alloys and soldering waves is critical to obtain reliable connection using soldering process. For electronic equipments, the optimal selection of soldering materials is determined by electrical, thermical and mechanical characteristics for a soldering connection. These characteristics are: a very good electrical and thermical conductivity, high mechanical resistance at vibrations, good resistance at corrosion and a good stability of these characteristics in time.

II. TECHNOLOGICAL CONDITIONS AND STANDARDIZATION OF ECOLOGICAL SOLDERING ALOYS

For a high reliability the ecological alloy must fulfilled some condition. These are:

a) chemical composition of alloy must be different from basic materials which compose the alloy;
b) inferior melting temperature (with 50°C) from basic metals;
c) a short melting interval, in contrary cases appear the separation trend between components with inferior melting point from components with superior melting point;
d) the viscous property and surface tension must be reduce; a good wetting capacity;
e) mechanical properties – tensile, shear, creep and fatigue as good is possible;
f) linear dilatation coefficient must be approximate equal with coefficient of basic metals;
g) structural stability;
h) reciprocal solubility between alloy components;

III. SELECTION CRITERIA FOR LEAD FREE SOLDER ALLOY

The necessity of using alloy with superior properties and characteristics is imperative because the entire electronic industries was build for SnPb alloy. Changing of all devices and technologies involve high costs. The selection criteria of alloys must take into account following aspects:

a) toxicity – principal reason for eliminate Pb from soldering technology is his toxicity for human body and environments. In table 1 is presented the toxicity of chemical elements which may be used as a substitute for Pb.
b) melting point - most simple selection criteria of alloy is melting point. The melting point must be appropriate to SnPb (183°C). Taking in to account this aspect we can classify the alloys vs. melting temperature:

I. *alloys with low melting temperature are used for specify soldering operation*

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Table 1

Element	Percentual concentration	Melting point at solid state (^0C)	Toxicity	Disponibility
Bi	0-100	138	No	Medium
Cd	0-100	188	High	Medium
In	0-100	117-150	No	Poor
Zn	0-90	198	No	Good
Au	0-82	218-310	No	Poor
Ga	0-100	18	High	Poor
Hg	0-100	140	High	Poor
Ag	10	221	No	Medium
Cu	3	227	No	High
Sb	5	232-236	No	Adeqvate

a) alloy with melting temperature bellow 180°C (table 2)

table 2

Alloy	Chemical composition	Melting temperature (^0C)
SnBi	Sn- 58 Bi	138
SnIn	Sn- 52 In Sn- 50 In	118 118-125
BiIn	Bi- 33 In	109

b) alloy with melting temperature between 180°C - 200°C (table 3)

Table 3

Alloy	Chemical composition	Melting temperature (^0C)
SnZn	Sn- 9 Zn	198,5
SnBiZn	Sn- 3 Bi- 8 Zn	189-199
SnBiIn	Sn-20 Bi-10 In	143-193

II. alloys with medium melting temperature - have the melting temperature above melting point of SnPb alloy (table 4). Most scientists consider these types of alloys the successors of SnPb because at wave soldering appears only minor difference during soldering process.

Table 4

Alloy	Chemical composition	Melting temperatur e (^0C)
SnAg	Sn- 3,5 Ag Sn- 2 Ag	221 221-226
SnCu	Sn-0,7 Cu	227
SnAgBi	Sn-3,5 Ag-3 Bi Sn-2 Ag-7,5 Bi	206-213 207-212
SnAgCu	Sn-3,8Ag-0,7Cu	217
SnAgCuSb	Sn-2Ag-0,8Cu-0,5Sb	216-222

The alloys from this categories binary, tertiary and quaternary chemical composition. Adding little amount of chemical elements leads to decreasing of alloy melting temperature, to a good wetting during soldering process and also increase solder reability.

III. alloy with high melting temperature (table 5)

Table 5

Alloy	Chemical composition	Melting temperature (^0C)
SnSb	Sn- 5 Sb	232-240
SnAu	Sn- 80 Au	280

c) reserve – is an important criteria because high reserve in environment involve low costs production (table 6)

Table 6

Element	Global production (tons)	Global capacity (tons)	Reserve quantity (tons)
Ag	13,500	15,000	1,500
Bi	4,000	8,000	4,000
Cu	8,000,000	10,200,000	2,200,000
Ga	30	80	50
In	120	> 240	120
Sb	78,200	122,300	44,100
Sn	160,000	241,000	81,000
Zn	6,900,000	7,600,000	700,000

d) low costs
e) physical properties above SnPb properties
f) resistance to aged
g) reability of soldering
h) wetting capacity

IV. MECHANICAL PROPERTIES

When an electronic device is in operation, the solder connections are subjected to mechanical stresses and strains. The primary cause of these stresses and strains arise from the fact that the electronic component and the board have different coefficients of thermal expansion [1]. An example of how these stresses are generated, in the case of flip chip packages, between the silicon die and the substrate, is shown in fig.1 If room temperature represents the unstrained conditions, then as the temperature of the system rises, the board expands more than the component, resulting in the solder ball connection being subjected to shear strain. As the system is switched 'on' and 'off', it is subjected to thermal cycling [2], resulting in the solder connection being subjected to cyclic shear

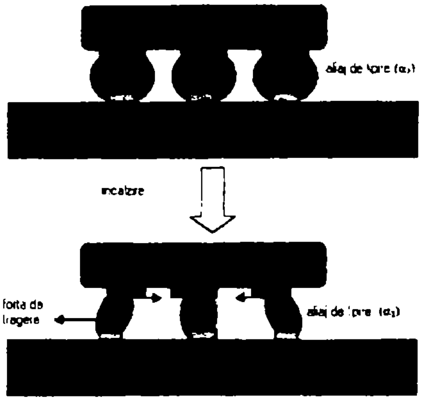

Fig.1. Stress generated between the silicon die and the substrate

stresses. The resultant shear strain will be determined by the shear modulus of the particular solder material. The solder connections are thus subjected to cyclic loading, and depending upon its fatigue life, the number of cycles before fatigue failure begins will be determined. Plastic deformation of the solder connection is also possible, if the shear strain due to differential thermal expansion exceeds the shear strain for yielding.

The solder joint can also be subjected to tensile loading, typically when the board or substrate is bent, as shown schematically in fig.2. This can happen during mechanical handling of the product, and sometimes when the finished product is clamped in the text fixtures for testing after assembly. The tensile properties such as yield strength, UTS and elastic modulus are therefore necessary to determine the extent of tensile deformation the solder connection can withstand without failure.

V. THERMAL PROPERTIES

a) Coefficient of thermal expansion.

A typical microelectronics assembly is made up of a large variety of materials, most notably, metals, polymers, polymer based composites and sometimes ceramics. During its service life the device goes through heat cycles because every time the device is powered, heat is generated due to IR heating.

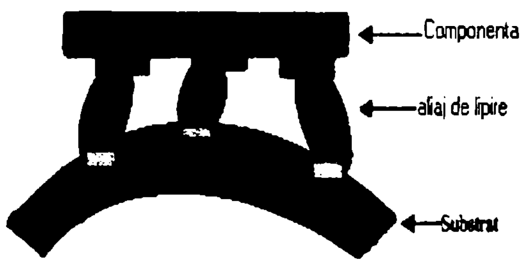

Fig.2. Solder Bumps (joints) subjected to tensile loading due to substrate flexing (bending) during handling of the assembly

Localized temperatures on the Si die itself can be as high as 300°C. If all of the components within the device have identical coefficients of thermal expansion (CTE), and heat transfer is instantaneous, then they will expand and contract at the same rate, and no thermally induced stress will arise. Unfortunately, this is not the case and thermally induced stresses do arise. Few data on CTE for Pb-free solders are available and these are summarized in table 7. CTE data for Si, Cu (used as lead frames),

Table 7

Solder composition	CTE ($\times 10^{-6}$/K)
Bi–42Sn	15.0 at 20°C
	14.0
In–48Sn (eutectic)	20.0 at 20°C
	2.0 at 20°C
Sn–3.5Ag	22.0
	30.0
	23.0
Sn–4.8Bi–3.4Ag	23.0
Sn–20In–2.8Ag	28.0 at 20°C
Sn–37Pb	21.0
In–3Ag	20.0
Si	2.6
Cu	16.0–18.0
Epoxies	60.0–80.0
FR-4	11.0–15.0

epoxies (the most common encapsulating material) and FR-4 (the most common PCB material) have also been included for reference purposes. Most of the solder alloys have CTE in the low 20×10^{-6}/K range with the exception of Bi–42Sn, which has a CTE of 15×10^{-6}/K.

b) Thermal conductivity

The heat generated by the die must be dissipated in order for the device to continue reliable operation. While the main pathway for heat dissipation is through the encapsulation material, the solder joints are also thought of as one pathway for heat dissipation. In high interconnect BGA devices that have more than 400 solder balls, it is a common

Table 8

Solder composition	Thermal conductivity (W/mK)
Bi–42Sn	21.0 at 85°C
In–48Sn (eutectic)	34.0 at 85°C
Sn–3.5Ag	33.0 at 85°C
	54.3 at 23.9°C (w/o contact resistance)
	36.2 at 23°C (w/o contact resistance)
	28.2 at 222.9°C
	28.6 at 246°C
	29.2 at 256°C
Sn–3.5Ag–1Zn	33.0 at 85°C
Sn–20In–2.8Ag	53.5 at 30°C
In–3Ag	73.0

practice to incorporate thermal solder balls, that do not serve any electrical function, to serve as a heat dissipation medium. The thermal conductivity of the solder is therefore a property of interest. The thermal conductivity data that were available for solder alloys are summarized in table 8. The room temperature thermal conductivity is approximately 50 W/mK. At higher temperatures the thermal conductivity decreases, as shown by the data for Sn–3.5Ag. Since transport via electron excitation is the primary mechanism for thermal conduction in metals, this result is not surprising.

VI. ELECTRICAL PROPERTIES

When the microelectronics device is functioning, the solder also serves as an electrical interconnect, i.e. all the electrical currents going into and out of the silicon device must pass through the solder connection [3].

In order to function adequately as an electrical interconnect, the electrical resistivity (table 9) is the property of interest. The electrical conductivity of the solders chosen must be sufficiently high to permit current flow for the geometry chosen, without IR heating. While this is very much a function of how the solder joint is designed, as the push for miniaturization continues, the electrical resistivity of the solder will continue to become more important. Solder interconnects can also be expected to undergo a certain amount of IR heating due to current flow. In addition, they can also be expected to experience a certain amount of heating due to the heat generated by the silicon device. As such, it is expected that temperatures at the solder joint can be as high as 125°C. The temperature coefficient of resistivity (TCR) therefore also becomes a property of interest. Ideally, the TCR should be as close to zero as possible, up to 125°C.

Table 9

Solder alloy	Resistivity (μΩ cm)
63Sn–37Pb	10, 14.4, 15
96.5Sn–3.5Ag	10, 12.3
58Bi–42Sn	30, 34.4, 34
50Sn–50In	14.7, 30
48Sn–52In	14.7

Lead frames	Resistivity (μΩ cm)
52Ni–48Fe	43.2
42Ni–58Fe	57
Cu–0.6Fe–0.05Mg–0.23Sn	2.65

Elements	Resistivity (μΩ cm)
Ag	1.59
Bi	115
Sn, Pb	10.1
Cu	1.73

The electrical resistivity of the Bi–Sn alloy is notably higher than the other alloys, all of which have electrical resistivities that are similar. The high resistivity value for Bi–Sn can be attributed to the high electrical resistivity of the elemental Bi, which is 115 μΩ cm, as compared to 10.1μΩ cm for Sn.

VII. CHEMICAL PROPERTIES

Three major chemical properties can affect the usage and long-term reliability of solders. They are: (a) solubility of Cu in the solder, (b) resistance to corrosion, and (c) oxidation behavior [4].

a) *Cu solubility.* When large baths of solder are used, such as in wave soldering, the solder bath tends to pick up Cu from the copper leads being soldered. When a critical Cu concentration in the bath is reached, the bath needs to be replaced. As such, the Cu pick up rate, and extent of Cu concentration in the bath before the bath needs to be replaced are important parameters and cost factors in soldering operations. The ability of solder baths to pick up Cu is directly dependent on the solubility of Cu in the major constituents.

b) *Corrosion.* Depending upon the particular design of the electronic component, and the manner in which it is mounted in a substrate or printed wiring board, the solder connection can be exposed to the atmosphere. This is the case with most SMT, PTH and BGA configurations. The solder is thus not only exposed to air, but also moisture and other corrosives such as chlorine and sulfur compounds. The ability of the solder to be able to withstand atmospheric corrosion is therefore relevant to the long-term reliability of solder joints.

In addition, solder alloys are electrically connected with other metallic components in the electronic device, most notably the copper conductors. Therefore, there is also the potential for galvanic induced corrosion of the solder, which could exacerbate any atmospheric corrosion that might be occurring.

VIII. CONCLUSIONS

Pending environmental legislation worldwide has provided an impetus towards the development of Pb-free solders. A relatively large number, approximately 70, of Pb-free solders have been proposed so far, by a combination of researchers and manufacturers. While a few of the alloys are patented, most are not. The majority of the alloys are based on Sn, In, and Bi being the primary component, with Sn being by far the most dominant. Materials selection studies thus far, albeit on a limited scale, indicate that the Sn rich compositions are the most likely candidates. A major impediment to adoption of In based solder compositions is the volatility of In prices.

IX. REFERENCES

[1]. D. Napp, Lead-free interconnect materials for the electronics industry, in: Proceedings of the 27th International SAMPE Technical Conference, Albuquerque, NM, 9–12 October 1995, p. 342.

[2]. J.S. Hwang, Solder Paste in Electronic Packaging, Van Nostrand Reinhold, New York, 1989.

[3]. J. Glazer, Metallurgy of low temperature Pb-free solders for electronic assembly *Int. Mater. Rev.* **40** 2 (1995), p. 67.

[4]. H.Cârstea, R.Mihăescu, Tehnologii ecologice de lipire în electronică, Editura de Vest, 2002.

[5]. H.Cârstea, A.Avram & colab., Tehnologii ecologice de lipire fără Pb în electronică, Workshop ETc – Solectron, Timisora, 2004.