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Comparison of lead-free solders

Why have we been using lead?

Melting point and working temperature
 Pure tin (Sn) has a melting point of 232°C.
 Working temperatures will be between 30 and 50°C higher. For some Printed Wire Board base materials and components these temperatures are already critical. The eutectic composition of Sn with 37% of lead (Pb) has a melting point of 183°C. This melting point allows for working temperatures of 250°C in wave soldering and 200-240°C for reflow soldering. Already for many years, the eutectic alloy is proving itself to be easy to work with. Chances of overheating are limited.

2. Availability

The world production of lead can easily cover the consumption in electronics manufacturing. Electronics manufacturing only takes $(0,5)^1$ percent of the world's production. The biggest consumers are the battery, paint and amunition industry.

3. Cost

Lead is very cheap:

Pb: 451 USD/ ton (London, 27/05/02) Sn: 4.130 USD/ ton (London, 27/05/02) Cu: 1.603 USD/ ton (London, 27/05/02)

Ag: 153.611 USD/ ton (€166,88 / kg) (Brussels, 27/05/02)

Lead has a higher specific gravity compared to other metals, this means that for a certain volume (solderjoint, solderbath) you will use more lead (in weight) than another metal. But its very low price compensates this.

Sn63Pb37 : 8,5 g/cc SnCu,SnAg, SnAgCu : +/- 7,3 g/cc

4. Stability

The Sn Pb alloy has proven itself very stable over many years.

Metallic impurities that are absorbed in the wave soldering bath do not influence the processability and mechanical characteristics of the alloy too much. Although maximum levels have been set for the different impurities, in practice, these levels are rarely surpassed. Except for Cu, but this can be filtered out. Impurities come into the bath through the boards and carriers that pass over it, the solder pot and nozzles themselves, any foreign material in contact with the alloy (spatulas for maintenance,...) or they are already present in the solderbars.

5. Mechanical properties

The Sn Pb is being used for many years in all levels of electronics, from consumer to aerospace. However automotive is looking for alloys with higher melting points because of the high temperatures under the hood of the engine. Another weak point of the alloy is limited creep strength.

It is hard to give absolute figures for the different mechanical properties because there are many parameters:

- grainstructure (determined by cooling)
- Intermetallic thickness (soldering time)
- impurities in the solder
- different testmethods and testconditions

tensile and shear strength: 20-40 N/mm² **Fatigue:** is the plastic deformation caused by T°-variations due to intermittent currents, leading to a cracked joint.

Creep: plastic deformation of the solderjoint when a permanent mechanical load or stress is applied. This can lead to a cracked solderjoint. E.g. too heavy component

6. Thermal and electrical conductivity
Thermal conductivity is determined by the heat dissipation capacity of the alloy. It is important that heat generated by electrical current is dissipated to the environment as fast as possible. Poor thermal conductivity will create higher temperatures (and also lower electrical conductivity) and could influence function of a circuit. Electrical conductivity is determined by the free movement of electrons and is for example influenced by grainstructure and temperature. The Sn Pb alloy has good thermal and electrical conductivity. Ag and Cu will even improve this. Bi and Sb will make it worse.

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What are the alternatives to replace lead?

Tin (Sn)

Lead-free alloys will be Sn based

- Low melting point compared to other metals 232°C
- Wettability on almost all other metals in question
- Availability
- Price

Disadvantages of tin (Sn)

- Agressive attacks the standard solder pots
- Sn whiskering: a apparently spontanious growth of Sn cristals which can lead to a short circuit
- Fast growth of the intermetallic² zone

Areas of use

- PWB manufacturing Chemical Tin is used as pad material
- Component manufacturing Pure Tin is used as lead finishing

Copper (Cu) Sn Cu (alloy)

- Eutectic alloy Sn99,3 Cu0,7: 227°C (non patented)
- Cheap alternative (ca. 1,5 x Sn Pb cost)
- Good alternative for wave soldering
- Less attack on solder pot (?)

Disadvantages of Sn Cu

 Cu needles and a strong oxide skin can hinder the solder flow. Possible increase of solder bridges. Wave solder machines not equiped with N² should use interflux[®] Anti-oxidant pellets to reduce the oxide skin

Silver (Ag) Sn Ag (alloy)

- Eutectic alloy Sn96,5 Ag3,5 : 221°C (non patented)
- Attacks standard solder pots
- Sensitive to Cu disolution in solder pots Cu disolution from PWB is high and fast growth of intermetallic² zone
- More expensive (ca. 2x Sn Pb cost)
- Limited Ag leaching from Ag holding component lead into the joint

Sn Ag Cu (alloy)

- Eutectic composition still under discussion: 217°C
- SnAg3.8Cu0.7 is patented. SnAg4Cu0.5 not patented
- Expensive
- Attacks stainless steel solder pots
- Not that sensitive to Cu absorption in wave soldering - limited Cu dissolution² from the board - limited Ag leaching from Ag containing component leads to the solderjoint
- Possible alternative for reflow and wave soldering
- Lead-free balls of BGA's and Flipchips are usually SnAgCu

Bismuth (Bi)

- Bismuth tends to embrittle an alloy, especially high bismuth solder alloys are very brittle
- In general, addition of Bismuth strengthens the alloy (tensile strength)
- Sn Bi alloys are not a viable replacement for wave soldering. If there are any Pb impurities in the component finishing, the danger of fillet lifting on through hole solderjoints exists

Sn Bi (alloy)

- Sn Bi is sometimes used as a leadfree component finishing (postmold plating)
- Adding Bi reduces the melting temperature of pure Sn(232°C)
- Eutectic alloy: Sn42 Bi58 : 138°C
- Bi slightly reduces thermal and electrical conductivity (not problematic)
- In a comparative test procedure of an independent organisation (ITRI Soldertec group)³ SnAgBi is graded lower than SnCu ,SnAg and SnAgCu

Antimony (Sb)

- Sb is an element that can be toxic. It is not really wise to replace toxic lead with another possible toxic product such as Sb, not if there are other possibilities
- Adding Sb to an alloy should give better mechanical properties
- Sb slightly reduces thermal and electrical conductivity (not problematic)

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- Sn Ag2,5 Cu0,8 Sb0,5 is a patented (Castin)alloy: 217-225°C
- In a comparative test procedure of an independant organisation (ITRI Soldertec group) SnAgCuSb is graded lower than SnAgCu

Indium (In)

- Very expensive (more expensive than Ag)
- Limited availability
- Poor mechanical properties

Zinc (Zn)

- Zn is a material that gives heavy oxides. When used in an alloy strong fluxes will be needed to solder with this alloy
- high level of dross formation in wave soldering
- high corrosion sensitivity

Sn Zn

- eutectic Sn Zn9: 199°C
- Used by the Japanese but in very controlled conditions and only for certain products
- In a comparative test procedure of an independent organisation (ITRI Soldertec group) SnZnBi is graded lowest of previous 6 Sn alloys

8. Conclusions

The most interesting alternative for reflow and wave soldering is an SnAgCu alloy. This is also recommended by several research organisations.

SnAg can be another option for reflow soldering as it has a higher tensile strength than SnAgCu.

For wave soldering, SnCu is a good alternative. It is low cost. It has inferior mechanical properties compared to SnAg and SnAgCu but in practice a wave soldered SnCu joint can be stronger than a reflow soldered SnAgCu joint. This because the wave solder bath absorbs metals that can have a negative effect on mechanical strength. In a reflow soldered joint these stay inside of the joint. SnCu has a thick oxide skin, when soldering under air it is necessary to use Interflux[®] Anti-Oxydant pellets.

References

^{1:} Joseph Fjelstad - Lead Free: Right or Wrong? | published in Circuit Assembly Jan.2001 pages106-113

^{2:} J.Bath, H.Ahluwalla, K.Chagger, K.Nimmo – Dissolution and intermetallic growth rates of rates of gold, silver, palladium,copper, iron and nickel in molten tin-lead and lead-free solders | soldertec

^{3 :} J.Bath, H.Ahluwalla, K.Chagger, K.Nimmo – Dissolution and intermetallic growth rates of rates of gold, silver, palladium,copper, iron and nickel in molten tin-lead and lead-free solders | soldertec