ECO SOLDER®

Lead-Free Soldering Technology

Features of Lead-Free Alloys and their Process Characteristics

The Trend Towards Lead-Free

Important Lead-Free Solder Alloys

The Assembly Process and Choosing the Optimal Alloy

Senju Metal Industry Co., Ltd

Guidance For Lead-Free Soldering Technology

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The Trend Towards Lead-Free / Important Lead-Free Solder Alloys / The Assembly Process and Choosing the Optimal Alloy

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Features of Lead-Free Alloys and their Process Characteristics

1 Introduction

In recent years, the use of lead, a heavy metal that can be harmful to the human body, has attracted a great deal of global attention.

A bill regulating the use of lead was introduced before the US Congress in 1990, but it was opposed by the industry due to the fact that an effective alternative material had not been developed. As a result, the bill was dropped.

The EU, on the other hand, is making efforts to regulate the use of lead under the banner of environmental conservation and the promotion of recycling. According to the EU Directive on Waste Electrical and Electronic Equipment , electrical appliances must be lead-free from 2008.

In Japan, according to the Domestic Electrical Appliance Recycling Act, tin and lead must be recycled. Lead use in particular is stringently controlled under the Waste Disposal and Public Cleaning Law, the Water-Pollution Prevention Law, and similar regulations.

We at Senju Metal Industry Co., Ltd. develop, manufacture, and market soldering material and associated equipment. With global environmental conservation and the realization of a resource-recirculating society as our goals, we have been working to promote the development and commercialization of lead-free solder.

Senju Metal Industry provides system solutions encompassing lead-free solder for electronic assembly, flux, production equipment, devices, and methods. If you are planning the introduction of lead-free solder in your production , you need to consult a solder manufacturer with experience. Our support staff are ready to assist you, and our comprehensive knowledge of lead-free soldering technology allows us to meet a wide range of customer needs.

Lead-Free Solder Spreads Worldwide

Within Japan	◆ Special Domestic Equipment Recycling Law — April 2001 ◆ Resource Effective-Utilization Promotion Law: Collection of used personal computers made mandatory — April 2001 ◆ Move toward standardization of Japan's lead-free solder (by the industrial, government, and academic sectors) — February 1998 to March 2000 Japan Welding Engineering Society (Examination of basic characteristics) Japan Electronic Industry Development Association (Examination of applied characteristics) ◆ Planned lead-free projects J I E P: Low-temperature lead-free solder development project — May 2000 to March 2002 I M S: Development of environment-conscious, next-generation bonding technology JWES: Proposal to JIS concerning Sn-Ag-Cu dual alloy (Sn-3.5 Ag-0.7 Cu and others) — Fiscal 2000 Efforts to establish standard test methods — Fiscal 2001 to 2002 ◆ Electrical-and electronic-equipment manufacturers: Voluntary activities with the goal of reducing the use of lead 2000 to 2001: Introduce one or more lead-free models per plant 2001 to 2002: Make all equipment lead-free ◆ Reducing lead used in automobiles; related MITI guidelines (excluding that used in automotive batteries) By the end of 2000: One-half of the 1996 level By the end of 2005: One-third of the 1996 level
Europe	◆ Making electrical equipment lead-free from January 1, 2008 onward EU Directive on Waste Electrical and Electronic Equipment
USA	◆ Industry led organization NEMI recommends Sn-3.9 Ag-0.6 Cu as the preferred alloy NEMI supports US based companies to prepare for lead-free soldering with 'a view' to the release of product by 2004. ◆ IPC Lead-Free Roadmap Lead-Free 1: Make solder lead-free Lead-Free 2: Lead-Free 1 + make printed-circuit-board surface treatment lead-free Lead-Free 3: Lead-Free 1 + Lead-Free 2 + make mounted-part surface treatment lead-free

2 Lead-free solder alloys

2-① Sn-Ag-Cu Alloy

Sn-Ag-Cu alloy plays the most important role in lead-free soldering, as it can be used to mount parts by reflow, flow, and manual soldering.

It has an excellent heat-resistance characteristic. Its creep resistance at 125°C is 3849 hrs compared with 1 hr for the SnPb alloy, thus indicating its good thermal fatigue/creep balance. Relatively free from the adverse effects of Ph contamination, the Sn-Ag-Cu alloy is a highly-reliable solder.

The alloy is easily worked into various shapes, and is supplied in many forms, including bar, paste, wire, cored wire, ball, and preforms. The Sn-Ag-Cu alloy is a nearly perfect solder choice.

Potential problems include a higher melting temperature, (36°C higher than that of conventional SnPb alloys), and in addition, its silver content means that its price is dependent on spot silver prices.

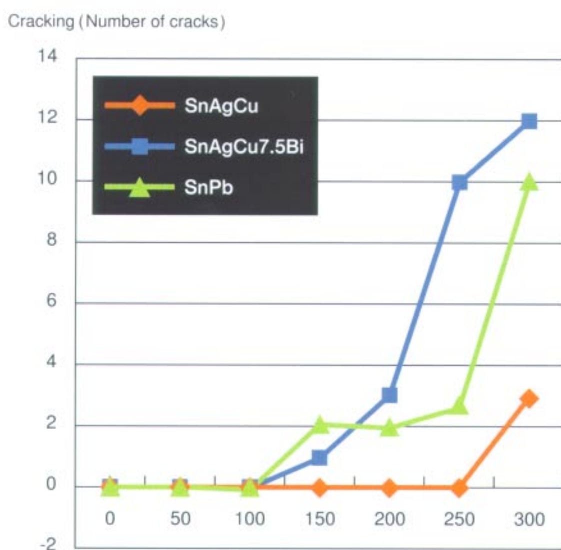

Fig.1 Solder Strength In Thermal Cycle Testing

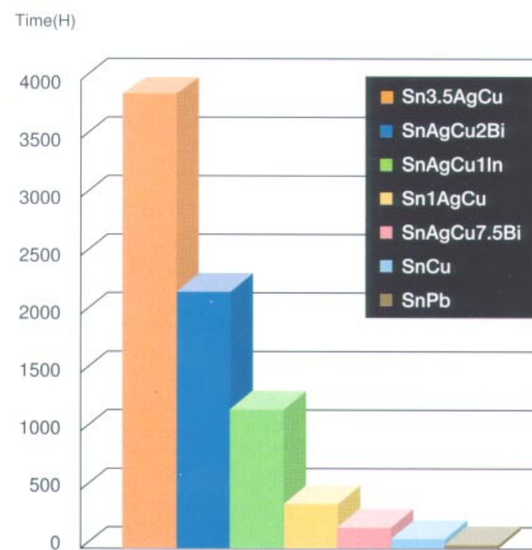

Fig.2 Creep Characteristics of Solder by Type

M705 was first marketed in April 2000. Its primary characteristics are listed below.

Table 1 Comparison of Sn-Ag-Cu Characteristics

	Alloy composition	Melting temperature (℃)	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)	Specific gravity	Coefficient of Thermal Expansion
M705	Sn-3.0Ag-0.5Cu	217 220	53.3	46	41.6	7.4	21.69
M31	Sn-3.5Ag-0.75Cu	217 219	53.0	47	45.1	7.4	21.32

2-② Sn–Cu Alloy

The major problems associated with this low-cost alloy are its high melting temperature, poor wettability, low resistance to thermal stress, and poor creep factor. Recently, due to its low cost, the Sn-Cu alloy has begun to find popular application in flow soldering of single-sided printed circuit boards that consume large amounts of solder. Studies have been conducted on this alloy with trace levels of Ni, P, and Ge to improve its oxidation characteristic. These elements, however, tend to react negatively with other elements on the solder surface. As a result, their amount tends to decrease as the amount of oxides increases. Adding Ge makes control of the alloy composition even more difficult.

2-3 Sn-Bi Alloy

The Sn-Bi eutectic has a low melting temperature of 139°C and is therefore well suited for mounting parts having low heat resistance. Bismuth, however, is not very ductile, and a case has been reported in which strong impact caused the soldered area to peel off. Examination of the peeled surface revealed a dimpled appearance of the Sn-Ag-Cu alloy, indicating that peeling is a form of ductile fracture caused by a force exceeding the material's ductile limits. In the Sn-Bi alloy, wall-to-wall fracture, which is apparently a form of brittle fracture, has been observed. Though all solders based on this alloy do not have the same problem, the user of a Sn-Bi alloy should consider this when deciding to use it.

When added to an alloy, Bi can decrease the melting temperature and enhance wettability by reducing surface tension. In recent years, an increasing number of solder products with from 1% to 3% bismuth have been marketed, though reliability and wettability must be considered if they are to be used.

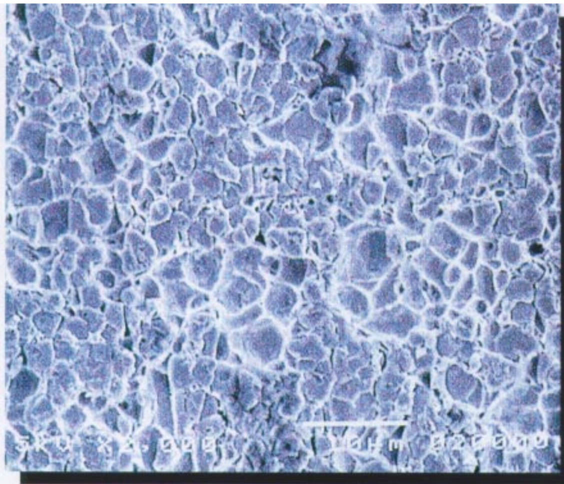

Photo 1 Peeled Surface of Sn-Ag-Cu Alloy

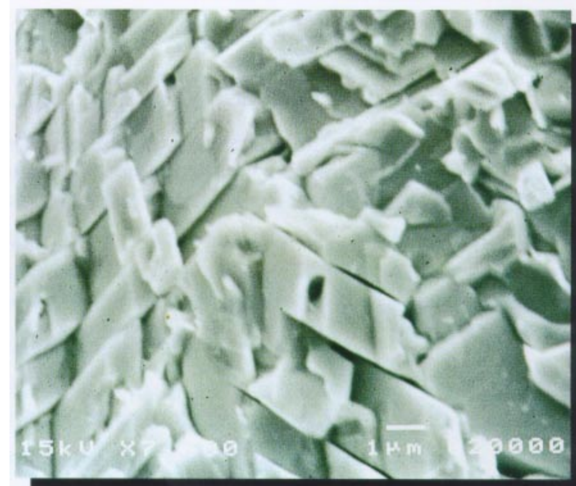

Photo 2 Peeled Surface of Sn-58Bi Alloy

2-4 Sn-Zn Alloy

The most noteworthy benefit of this alloy is its melting temperature. Although there are many lead-free solders on the market, the melting temperature of the Sn-Zn alloy is closest to that of the SnPb alloy. The melting temperature of the Sn-Zn eutectic is 199'C. With the Sn-8 Zn-3 Bi type, the solidus temperature is low, at 189°C, and the working temperature can therefore be kept low as well. The Sn-Zn alloy is thus advantageous as components that are currently used with Sn-Pb solder can also be used with Sn-Zn alloy.

However as Zn has traditionally been treated as an impurity in the Sn-Pb solder, many problems remain to be solved.

Whereas reflow in air using solder paste is the most commonly used soldering method today, a number of studies on reflow in an N2 atmosphere are underway.

Wettability is a problem with Zn, because it forms a strong, stable oxide film. Although this problem can possibly be solved by a new flux, a N2 gas atmosphere is almost certainly required.

The strong ionization tendency of Zn means high reactivity with organic acids, and this degrades storage stability. These properties also produce a short stencil life.

An important point in the application of the Sn-Zn alloy is the establishment of a recycling system. When it contaminates other metals, Zn hinders recycling. It is therefore necessary to establish a recycling system for the Sn-Zn alloy put into practical use, and provide a reliable collection route for commodities and equipment using the alloy.

3 Problems associated with reflow soldering and solutions

Table 2 Major Problems with Lead-Free Reflow Soldering and their Solutions

	Problem	Remedy
1	Inconsistent reflow-furnace temperature	Investigate low ΔT and thermal stability
2	Pb contamination	Avoid Bi (do not produce BiPb)
3	Low wettability	Improve flux; use N_2 reflow
4	Tombstoning	Conduct thermal analysis; use twin-peak product
5	Reduced self-alignment	Adjust and maintain mounting machine

3-1 Inconsistent reflow-furnace temperature

Lead-free solder has a high melting temperature, and its reflow temperature is only slightly higher, therefore the PCB temperature differential, ΔT, is critical. Measuring the ΔT produced by the existing equipment will show if the temperature differential needs to be reduced and if the required reduction is achievable with the existing equipment.

One way of decreasing the temperature differential ΔT is by elevating the preheat temperature so as to reduce temperature differentials in preheat and in the reflow zone. This however can cause thermal deterioration of the flux, depending on the combination of materials used, and consequently can even increase the number of unfused solder balls and degrade wettability. The thermal profile should be evaluated very carefully.

Photo 3 Effect of Different Pre-Heat Conditions (SnAgCu-RMA)

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4 Problems associated with flow soldering and solutions

Table 3 Major Problems with Lead-Free Flow Soldering

Problem	Current state
Lift-off	Occurs when the time after soldering until solidification is inconsistent due to the temperature limit of the alloy, as in a multilayer board with a large heat capacity.
Shrinkage cavity	Often occurs in large areas on single-sided boards where thick solder solidifies unevenly.
Insufficient solder wicking in plated through holes	A high solder melting temperature, which is close to the soldering temperature, and a smaller spreading capacity than that of Sn-Pb alloy combine to cause poor wicking in plated through-holes.
Increased oxide	The main constituent is Sn, which has high oxidation energy. Since the melting temperature is close to the working temperature, solder that drops from the jet-flow outlet rapidly cools and solidifies. Once the oxide begins to accumulate, a very active cycle starts, with one layer initiating oxidation in the next.

Here, we consider lift-off in particular. As shown in the magnified photo, lift-off is a state in which solder does not adhere to the land.

It occurs primarily in combinations of multilayer printed circuit boards that have a high heat capacity, and with alloys with wide melting-temperature range.

Solder shrinks when it solidifies causing lift-off where low- and high-melting points occur.

To prevent or reduce this, the melting-temperature range of the solder should be as narrow as possible, the heat capacity of the printed circuit board should be as low as possible, and an appropriate rapid cooling method should be employed.

This graph illustrates the tendency of lift-off to occur in our products, L21 (Sn-2 Ag-0.5 Cu-7.5 Bi) and M31 (Sn-3.5 Ag-0.75 Cu).

With the combination of M31, Sn-Ag-Cu alloy, and Sn-plated leads, lift-off does not develop even if the solder is annealed, whereas L21 containing 7.5 Bi causes lift-off at a higher rate. Although rapid cooling greatly decreases the occurrence of lift-off, combining it with the use of Sn-Pb-plated leads is unlikely to be a means of complete prevention.

The results of the experiment, nevertheless, suggests that rapid cooling by causing Sn-Ag-Cu alloy to contact a cooling liquid, along with the choice of the optimal surface-treatment method for leads, can reduce lift-off to an acceptable level for commercial applications.

[Test circuit board: FR-4 / Cu-TH / ∅1.0 hole and ∅1.9 land; part: DIP-IC / SnPb-plated and Sn-plated)

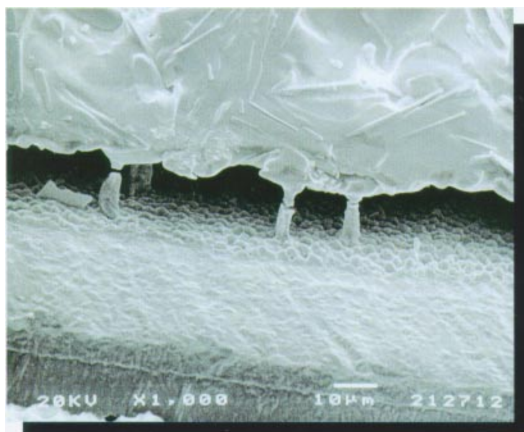


Photo 4 Magnified Lift-off (1000x)

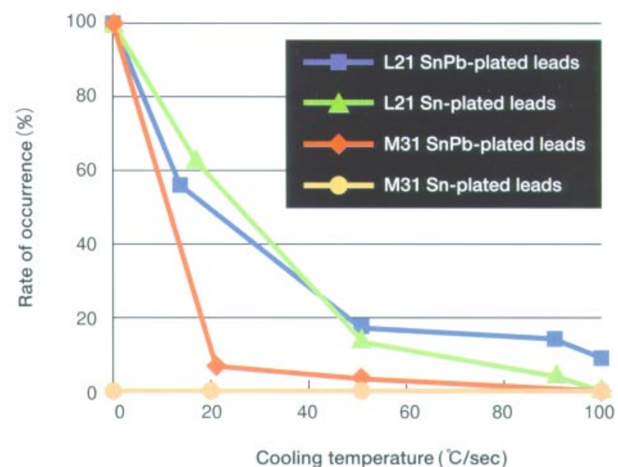


Fig 3 Cooling Rate and Percentage of Lift-off Occurrence

5 The assembly process and choosing the optimal alloy

For flow soldering, the Sn-Cu alloy is considered the best choice for single-sided printed circuit boards due to its relatively low cost, though its melting temperature is high. The Sn-Ag-Cu alloy should be used for multilayer printed circuit boards due to its higher reliability.

For reflow soldering, the Sn-Ag-Cu alloy is the best choice due to its superiority in terms of reliability for high-density printed circuit boards assembly.

When it is necessary to lower the melting temperature, because components have low heat resistance, small amounts of Bi and In are added. However, Bi poses a problem with ductility, and In is a scarce resource and therefore costly.
When selecting a lead-free alternative it is recommended that cost and availability are considered, along with the technical features related to joint reliability and the possibilities for recycling.

Table 4 Mounting Process and Alloy

Alloy	Item	Flow soldering	Reflow soldering	Hand soldering
Sn-Cu	M12	○	△	—
	M20	○	△	○
	M35	○	△	○
Sn-Ag	M30	○	○	○
Sn-Ag-Cu	M31	○	○	○
	M34	△	○	○
	M702	○	○	—
	M704	○	○	—
	M705	○	○	○
Sn-Ag-Cu-Bi	SA2515	○	○	○
	M41	○	○	※
	M42	△	○	※
Sn-Bi	L20	○	△	—
Sn-Bi-Ag	L23	○	△	—
Sn-Ag-Cu-In	M51	—	○	—
Sn-Zn	L10	—	○	—
Sn-Zn-Bi	L11	—	○	—

O: Recommended Δ: Difficult to achieve optimum results ⁎ : Special product required -please contact us for details

6 Marking printed circuit boards with the name of the alloy used

Recycling requires a minimum cost principle, and at present lead-free alloys are becoming increasingly diversified in type. We therefore propose marking the printed circuit boards with the type of solder it contains as a means of promoting efficient recycling and therefore achieving a resource-recycling society in the near future.

The marking methods could include screening, etching, labeling, and the like. Markings should include element symbols, chemical composition, solder alloy number, and so on.

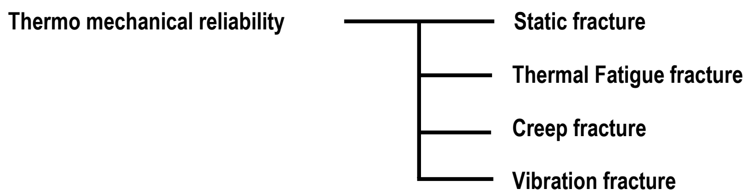
Such marking will assist in the initial classification of materials to be recycled, thus enabling the efficient reuse of resources. It also helps prevent the disposal of useful resources due to the contamination with special elements.

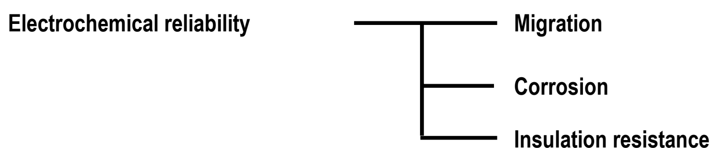
7 Considerations for putting lead-free solder into commercial use

Supplying good products at a low cost assures satisfied and loyal customers. The items specified below should be taken into consideration to enable the efficient migration from conventional solders to lead-free types.

- Reliability is an absolute requirement. The right decision now, about Sn-Ag-Cu alloy will help you do your part to prevent Pb contamination.
- When using a Bi-containing alloy, confirm in advance that its reliability has not been compromised by Pb contamination.
- Seek the optimum process conditions using the existing equipment.
- If your existing equipment will be difficult to convert to lead-free solders, perhaps you should consider modifying or upgrading your equipment.
- Request that manufacturers of low-heat resistance parts improve the heat resistance of their products.
- To improve wettability, consider surface pre-treatment (Pb-free solder plating) , use of the N2 process, and use of a high performance flux.
- To ensure easy recycling, attempt to "design-in" recyclability. Cost increases may be minimized through economies of scale.
- Set conditions taking into consideration the narrow gap between the melting and working temperatures, as well as inconsistencies in the process.
- Work toward global standardization by publicizing and sharing alloy data.

Checking reliability





8 Conclusion

Printed circuit boards, equipment, conditions, and the like vary by production line and plant. Each line and plant, therefore, should identify the best solution for itself through trial and error. When a reasonable conclusion is reached, standardization should begin and mass production should be launched.

We at Senju Metal Industry Co., Ltd. consider fostering environmental conservation in the 21st century to be our duty to society. With our large and diverse research staff, we will work to meet all the social needs. If you are planning to introduce lead-free solder, please feel free to contact us and take advantage of our wide experiences of the different alloys and processes.

Data Typical Lead-Free Solders and Product Lineups

Item	Alloy compositions	Melting points Solid phase／Liquid phase		Bar	Wire	Flux-contained	Ball	Paste
M-Series (solid phase temperature : 200 to 250℃)								
M10	Sn／5.0Sb	240	243	○	○			
M12	Sn／0.7Cu／0.3Sb	227	229	○	○			
M20	Sn／0.75Cu	227		○	○	○	○	○
M30	Sn／3.5Ag	221		○	○	○	○	○
M31	Sn／3.5Ag／0.75Cu	217	219	○	○	○	○	○
M34	Sn／1.0Ag／0.5Cu	217	227	○	○		○	○
M35	Sn／0.7Cu／0.3Ag	217	227	○	○		○	
SA2515	Sn／2.5Ag／1.0Bi／0.5Cu	214	221	○				○
M41	Sn／2.0Ag／0.5Cu／2.0Bi	211	221	○				※
M42	Sn／2.0Ag／0.75Cu／3.0Bi	207	218	○				※
M51	Sn／3.0Ag／0.7Cu／1.0In	214	217	○	○		○	○
M702	Sn／3.0Ag／0.7Cu	217	219	○	○	○	○	○
M704	Sn／3.35Ag／0.7Cu／0.3Sb	218	220	○			○	○
M705	Sn／3.0Ag／0.5Cu	217	220	○	○	○	○	○
L-Series (solid phase temperature : below 200℃)								
L11	Sn／7.5Zn／3.0Bi	190	197	○				○
L20	Sn／58Bi	139		○				○
L21	Sn／2.0Ag／0.5Cu／7.5Bi	189	213	○				○
L23	Sn／57Bi／1.0Ag	138	204	○				○

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