Identifying Reliable Applications for the Tin-Zinc Eutectic in Electrical and Electronic Assemblies

Keith Sweatman¹, Takashi Nozu¹, Alberto Kaufman², Tetsuro Nishimura¹ 1.Nihon Superior Co., Ltd. Osaka, Japan, 2. IKA, Haifa, Israel

Abstract

With a melting point of 199°C, about 20°C lower than the liquidus temperature of SAC305 the Sn-Zn eutectic (Sn~9% Zn) appears to be an attractive candidate as a Pb-free solder. With, at July 2010 market prices, a raw material cost less than half that of SAC305 the Sn-Zn eutectic also has the attraction of substantial cost savings. And, in contrast with Ag, Zn is a relatively abundant element of low toxicity with a comparatively low impact on the environment. The mechanical properties of Sn-Zn alloys are more than adequate in most situations and they have found widespread application in specialised areas such as the joining of high voltage aluminium cables. The Sn-Zn eutectic has, however, found only limited application as a Pb-free solder in electronic assemblies because of early mechanical failure on Cu substrates where the substantial difference in electronegative potential drives galvanic corrosion in the presence of even quite low levels of moisture and ionic contaminants. In this paper the authors report studies that indicate that with the use of a microalloying addition of Mn joint integrity can be maintained on some of the substrates commonly encountered in electronics assembly. Sn-Zn alloy solder joints were exposed to high temperature (150°C) and humid heat (85°C/85% RH) for up to 1000 hours, the mechanical properties measured and the microstructure monitored. Joints were also exposed to salt water and to electric current under conditions of heat and humidity. These studies indicate that there is potential for wider use of alloys based around the Sn-Zn eutectic as solders in electronic applications.

Key words: Pb-free, Sn-Zn, Corrosion, CTE, Shrinkage Stress

Introduction

Nearly five years after the implementation of the European Union RoHS Directive mandating the use of Pb-free solders in consumer electronics sold in that market it is becoming increasingly clear that simple ternary alloys based around the Sn-Ag-Cu eutectic widely endorsed by industry associations and consortia cannot deliver everything that the electronics industry requires in a solder in terms of cost and performance. In the first instance the industry responded to that reality by developing variations around that Sn-Ag-Cu eutectic. The cost of the 3 - 4% Ag required to get the 217° C solidus temperature that was one of the main reasons for choosing the Sn-Ag-Cu eutectic has prompted the industry to reduce the Ag content as low as 0.1% Ag, and even use Sn-Cu alloys with no Ag, and accept the consequent 10°C higher solidus temperature. The non-eutectic behavior of nominally eutectic alloys which can result in dull cracked solder fillets is being addressed by trace additions of a third element such as Ni to Sn-Cu and a fourth element such as Mn to Sn-Ag-Cu. These "microalloying" additions appear to work by facilitating the nucleation of the Cu_6Sn_5 intermetallic phase of the eutectic, which then acts a nucleant for Sn so that so that eutectic solidification can proceed. In the Sn-Ag-Cu system this facilitation of nucleation prevents the extreme undercooling that otherwise creates conditions under which the formation of the undesirable primary Ag₃Sn phase is favoured. Microalloying is also being use to improve the resistance of Pb-free solder joints to drop impact, a property that has been found to be important for the portable devices that make up an increasing proportion of the consumer electronics market and which has been found to be lacking in the unmodified Sn-Ag-Cu eutectic.

The issues that have prompted the introduction of variants to the Sn-Ag-Cu and Sn-Cu alloys have also prompted the exploration of other alloy systems. However, the industry has had to accept that nature had provided only a very limited number of elements that can be used as the basis for alloys with melting points and wetting properties that make them candidates as solders that can be used in electrical and electronic circuitry. Those elements include bismuth, indium, and Sn all of which form eutectics with tin, the element which, because it forms intermetallics with and hence can wet most of the substrate metals of interest in electrical and electronic circuitry, is an essential constituent of solders. In the study reported here some of the properties relevant to the performance of alloys based around the Sn-Zn eutectic as solders in a range of applications were measured and compared with some other alloys that are already widely used as Pb-free solders.

Background

The binary Sn-Zn system is a simple eutectic with, in the solid state, almost no solubility of Sn in Zn and only very limited solubility of Zn in Sn (Figure 1). The Sn-Zn eutectic and alloys based around it have a long record of use as a soft solder for two reasons. The eutectic at about 8.8% Sn has a melting point of only 198.5°C well within the range and its electronegative potential is sufficiently close to that of aluminium that the risk of galvanic corrosion that is otherwise a problem with soldered joints on that metal and its alloys is minimized. However, its use in electrical and electronics assembly has come into consideration only since it has become necessary to find Pb-free alloys that have properties that might make them suitable as replacements for Pb-containing solders. Initial experience with the Sn-Zn eutectic has, however, been disappointing. This alloy is more prone to oxidation than Sn-Cu and Sn-Ag Cu alloys when exposed to

air while in the molten state during the soldering process. For this reason it cannot be used in wave soldering processes because of the excessive production of a sticky dross that cannot be controlled by the use of antioxidant additives such as phosphorus and germanium that are effective in solders that do not contain Zn. That susceptibility to oxidation means that Sn-Zn solders can be used only as a solder pastes and to a limited extent in the form of solder wire. However, even in solder paste the chemical activity of the Zn is a problem because it tends to react with the flux medium. The consequence of that reaction is both an increase in the viscosity of the paste during storage, which makes it difficult to print and a reduction in the activity of flux that results in incomplete reflow and poor wetting of joint substrates. If alloys based around the Sn-Zn system are to find application as solders for electrical and electronic assembly a way would have to be found of limiting the extent to which the Zn can participate in corrosive reactions.

An approach to this problem that has been proposed is microalloying with a ternary addition that will have an affinity with the Zn and thus reduce its activity towards other elements. Candidate elements that emerge from a review of the known binary Zn systems on this basis are transition metals Mn, Cu, Ni and Fe. Of these Mn seems to have the greatest affinity for Zn forming at least10 known intermetallic compounds (Figure 2) while having the least affinity with Sn. The hypothesis that because of this strong affinity with Zn that a Mn will have beneficial effects on the performance of the solders based on the Sn-Zn eutectic is the basis of a patent [1]



Figure 1: Sn-Zn equilibrium phase diagram

Alloy Microstructure

On the basis that the first intermetallic formed when Mn is added to Zn is $MnZn_{13}$ a series of Sn alloys with increasing Zn content was prepared with a Mn addition in the atomic proportion Mn:Zn of 1:13. The most perfect eutectic microstructure (i.e. no primary Sn or Zn phases) was achieved with the alloy Sn-7.66Zn-0.49Mn (Figure 3). There were small areas of primary tin in the alloy Sn-7.20Zn-0.46Mn (Figure 4) and an acicular primary Zn phase in the alloy Sn-8.26Zn-0.53Mn (Figure, 5). In the microstructure of the Sn-7.66Zn without Mn there is a significant proportion of primary Sn (Figure. 6) so it appears that the Mn addition suppresses the formation of primary tin dendrites. On the basis of experience with other binary systems it is hypothesised that the Mn works by facilitating the nucleation of one of the eutectic phases so that the undercooling that would otherwise favour the formation of primary tin dendrites does not occur.

Examination of the interface between SnZnMn alloys and Cu substrate indicates only a diffusion zone rather than the usual Cu_6Sn_5 intermetallic and the thickness of this diffusion zone decreases from about 5µm with a hypoeutectic alloy (Figure 7) to around 2.5µm with the eutectic alloy (Figure 8) and remains at that thickness as the Zn content increases provided there is a commensurate increase in the Mn addition (Figure 9).



Wetting Behavior

Perhaps because the presence of Mn in the alloy appears to tip the thermodynamic balance away from the formation of Cu_6Sn_5 at the solder Cu interface the wetting of the Sn-Zn alloys, as measured by wetting angle with a low-solids alcohol-based flux, is dramatically improved by the Mn addition (Figures 10 and 11)



Figure 4. Sn-7.20Zn-0.46Mn. (x200). Some primary Sn in the microstructure



Figure 5. Sn-8.26Zn-0.53Mn (x200) Primary Zn phase in the microstructure



Figure 6. Sn-7.66Zn (x200) Without Mn primary Sn dendrites appear in the microstructure.



Figure 7. Interface (B) between Sn-6.71Zn-0.43Mn (C) and Cu substrate (A). (x1000)



Figure 8. Interface (B) between Sn-7.66Zn-0.49Mn (C) and Cu substrate (A) (x1000)



Figure 9. Interface (B) between Sn-13.43Zn-0.86Mn (C) and Cu substrate (A) (x1000).



Figure 10. Contact angles on Cu substrate: left Sn-7.66Zn, right Sn-7.66Zn-0.49Mn



Figure 11. Contact angle as a function of Zn content showing the effect of Mn addition

Alloys Tested

On the basis of result of the preliminary testing that indicated some significant and possibly beneficial effects of a trace addition of Mn on the Sn-Zn eutectic these alloys were subjected to a wide range of tests that would provide an indication of their suitability as solders for use in the production of electrical and electronic circuitry. To provide a benchmark against which the performance of the SnZnMn alloys could be compared a range of other alloys, including some that enjoy widespread commercial application were included in the program. The main solder alloys tested are listed in Table 1 but because of issues of availability some testing was done with alloys of slightly different compositions.

Experimental Methods and Results

Alloys based about the Sn-Zn eutectic with and without varying levels of Mn were subjected to a range of tests which would provide an indication of where they fitted in the general landscape of Pb-free solders. The two widely used Pb-free solders against which the Sn-Zn alloys were benchmarked were the Sn-3.0% Ag-0.5% Cu alloy commonly known by the generic name"SAC305" and the Sn-0.7% Cu-0.05% Ni alloy with the addition of Ge as an antioxidant is marketed under the name "SN100C[®]" In some cases comparisons were also made with Sn-37% Pb.

Designation	Composition
SnZnMn-1*	Sn-7.4Zn+<0.01Mn
SnZnMn-2	Sn-7.8Zn-0.003Mn
SnZnMn-3	Sn-7.0Zn-0.007Mn
SnZnMn-4	Sn-7.5Zn-0.26Mn
SnZnMn-5	Sn-7.4Zn-0.006Mn
Sn7Zn	Sn-7Zn
Sn9Zn	Sn-9Zn

Table 1. Alloys Subjected to Bond Strength Testing

* This is a proprietary alloy marketed by LFSMD under the brand name "IKAlloyTM" [2]

Measurement of Bond Strength-Tensile

Samples of the alloys listed in Table 1 were soldered to a Cu plate and a nail attached to the top by a strong epoxy adhesive (Figure 12). There were three duplicates for each alloy. Solder joint were subject to tensile testing before and after ageing at 150° C or exposure to 85° C/85%RH for 500 hours and the location and nature of the failure noted.



Figure 12: Bond pull strength set-up



Figure 13: Separation at the solder/Cu interface in SnZnMn-3 alloy

For the joints in the as-soldered condition all failures occurred at or near the bond between the solder and the nail. That was also the case after 500 hours elevated temperature ageing except for SnZnMn-3 which suffered failure at the Cu/solder interface (Figure 13). After 500 hours heat and humidity failure through the solder occurred only with the Sn9Zn and Sn7Zn alloys

Measurement of Bond Strength-Shear

Chip resistors soldered onto a test vehicle (Figure 14) with solder paste made up with the alloys SnZnMn-1 and Sn9Zn their shear strength measured before and after being subjected to 1000 30 minute cycles of $-40 - +80^{\circ}C$.

		-	100	100		-	-	-	-	-
	-		100	-	-	-		-	-	-
			-	-	-				-	-
			-	-	-	-		-	-	
			-					-	-	
						-	-			
		-	101						-	-
	-	***					-			
				-	-			-	-	-

Figure 14: Bond shear strength test vehicle

The results (Figure 15) indicate no significant advantage for the alloy containing the Mn addition. Joints appear to be of comparable quality (Figure 16)

Tensile Testing of Bulk Solder

Approximately 10mm square cast test pieces of the alloy SnZnMn-3 were tensile tested at room temperature at strain rates of 1mm/minute and 10mm/minute and the results compared with those for similar test pieces of Sn9Zn and Sn7Zn. The results (Figures 17 and 18) show that at 1mm/min the Sn9Zn begins plastic deformation at a significantly lower stress than the other two alloys but was more ductile with a 76% elongation. At the same strain rate the results for the other two alloys is similar with a higher flow stress but with ductility reduced by around 50%. At 10mm/minute the Sn9Zn still starts plastic flow at a stress slightly lower than Sn7Zn but now shows less ductility

Thermal Cycling of Solder Joints

The terminations of a connector (Figure 19) were hand soldered into a test vehicle with alloys SnZnMn-1, SnZnMn-4, and Sn9Zn and subjected to 1000 30 minute cycles of -40 - +80°C and visually inspected for damage. All joints survived with no significant damage apparent (Figure 20).



Figure 15: Comparison of shear strength to chip joint after 1000 cycles of -40 - +80°C.



Figure 16: Comparison of quality of joints to 2125 chip capacitor.



Figure 17: Results of tensile testing bulk solders



Figure 18: Flow stress and elongation comparison.



Figure 19: Connector for testing solders in thermal cycling

Wetting

The effect of an Mn addition on the wetting of substrate metals was checked by making a solder pastes with a flux medium specifically formulated for use with SnZn alloys and Sn9Zn and Sn2nMn-1 powder. These pastes were reflowed onto Cu, brass and Ni substrates at 230°C. No significant beneficial effect of the Mn addition was observed and Figure 21 is representative of the results obtained.



SnZnMn-4

Figure 20: Solder fillets after 1000

30 minute cycles of $-40 - +80^{\circ}$ C.



Figure 21: Comparison of wetting of Cu by solder paste formulated with the indicated alloy powder.

Surface Discoloration

The surface of cast disks of each solder were compared before and after exposure to 7 hours of 85°C/85%RH. All alloys suffered discolouration with the test pieces in Figure 22 representative. Discolouration of the Zn-containing alloys was slightly greater than that of the SnAgCu and SnCuNi alloys.



Figure 22: SnZnMn-3 alloy before (left) and after exposure to 7 hours of 85°C/85%RH.

Measurement of Electronegative Potential

The difference in electronegative potential is the driving force for the galvanic corrosion that has been identified as the main cause of failure of Sn-Zn solders, The electrode potential of a selection of SnZn and SnZnMn alloys applied by dip soldering to Cu, Ag and aluminum substrates was measured along with the substrate alloy. The SnAgCu an SnCuNi alloys were also included for comparison. The set up in which the potentials were measured is pictured schematically in Figure 23.

Potentials were measured over a one hour period and a typical result is presented in Figure 24.



Figure 23: Set up for measurement of electronegative potentials



Figure 24: Plot of electronegative potential as function of time or a selection of solders on a Ag substrate after 60 minutes.

Since the driving force for corrosion is the difference in electronegative potential between the solder and the substrate the results are presented in this form in Figure 25. Even with the Mn addition the Zn-containing solders have greater difference in electronegative potential compared with the substrate than the SnAgCu and SnCuNi alloys.

Surface Corrosion

The alloys listed in Table 1 were applied to a Cu substrate in a form similar to that in Figure 12, exposed to 85C/85%RH for 500 hours and then cross sectioned for examination of the solder/Cu interface and to assess the extent of surface corrosion.

There was considerable variation in the degree of corrosion (Figure 26). While there was deep intergranular corrosion of the Sn9Zn and Sn7Zn alloys there was substantially less corrosion on the SnZnMn-1 which has an addition of 0.006% Mn. While intergranular corrosion extended to a depth of about 500 μ m in the Sn9Zn and Sn7Zn alloys in the SnZnMn-1 alloy the intergranular corrosion did not extend beyond about 20 μ m which suggests that the Mn has a significant inhibiting effect.

CTE and Elastic Modulus

The coefficient of thermal expansion was measured over three temperature ranges of relevance to reliability assessment with a Mac Science TD5000S dilatometer (Table 2). Using the elastic modulus estimated from the tensile stress strain plot the stress that each solder could generate as a consequence of the contraction that occurs between the freezing point of the solder and room temperature. (Table 3, Figure 27)



Figure 25: Electronegative potential differences between solder alloys and substrate.



Figure 26: SEM of cross-sections o solder on Cu substrate after 500 hours of 85°C/85%RH.

Allov	CTE (ppm)					
- 1	30-80°C 80-130°C		130-180°C			
SnAgCu	26.6	27.2	26.7			
SnCuNi	24.4	25.4	26.5			
Sn9Zn	22.7	23.3	24.3			
Sn37Pb	25.5	28.5	28.0			
SnZnMn-1	22.3	23.5	25.5			

Table 2: Coefficients of thermal expansion



Figure 27: Stress generated by shrinkage during cooling from the freezing point to room temperature.

Alloy	Elastic Modulus (N/mm ²)	Melting Point °C	Shrinkage Freezing Point to 20°C; ΔL/L	Shrinkage Stress (N/mm ²)
SnAgCu	3179.9	217	0.00527	16.8
SnCuNi	887.5	227	0.00530	4.7
Sn9Zn	869.4	198	0.00417	3.6
Sn37Pb	766.1	183	0.00444	3.4
SnZnMn- 1	713.3	198	0.00425	3.0

Table 3: Calculated shrinkage stress on cooling from the freezing point to 20°C

Discussion

The exploratory studies reported here confirm the general experience that solders based about the Sn-Zn eutectic are more susceptible to intergranular corrosion than the commonly used Pb-free solders based on the Sn-Cu and Sn-Ag-Cu eutectics. The greater difference between the electronegative potential of these solders and common substrates is certainly a factor in driving that corrosion (Figure 25). However, as claimed in the patent [1], microalloying with Mn does appear to reduce significantly the extent of corrosion that occurs under conditions of heat and humidity. The depth to which intergranular corrosion penetrates after 500 hours exposure to 85C/85%RH is reduced by a factor of 25 or more. In regard to mechanical properties the apparent effect of the Mn effect on CTE and elastic modulus is notable.

Conclusions

The improved resistance to corrosion that seems to be achieve by microalloying with Mn opens up the possibility of alloys based around the Sn-Zn eutectic finding wider application in electrical and electronic assemblies. The lower shrinkage stress as the alloy cools from its freezing point might make possible more reliable joints to brittle substrates. Investigation of that possibility will be the basis for future work on this alloy system.

Acknowledgments

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References

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Identifying Reliable Applications for the Tin-Zinc Eutectic in Electrical and Electronic Assemblies

Keith Sweatman¹, Takashi Nozu¹, Alberto Kaufman², Tetsuro Nishimura¹ 1.Nihon Superior Co., Ltd. Osaka, Japan, 2. LFSMD, Nesher, Israel

your partner for soldering solution





Identifying Reliable Applications for the Tin-Zinc Eutectic in Electrical and Electronic Assemblies

An alloy based on a Mn addition of a few tens of ppm Mn to Sn7Zn has been subjected to intensive study with a view to determining whether it has potential as a commercial Pb-free solder.





Outline

- Why consider SnZn?
- Microstructure of SnZn alloys with trace additions of Mn
- The distribution of Mn in SnZn alloys
- Some mechanical properties of the SnZn alloys
- Detailed observation of surface oxidation and galvanic corrosion of SnZn alloys on various substrates
- Observation of the interface between SnZn alloys and various substrates after aging
- Comparison of Ag dissolution by SnZn alloys with that by other common solders
- Conclusions



Why look at tin-zinc?





2. Alloys based around the tin-zinc eutectic have a long history of successful use in soldering aluminum



Why look at tin-zinc?

Tin	US\$/tonne	32,600
Lead	US\$/tonne	2,877
Zinc	US\$/tonne	2,440
Copper	US\$/tonne	9,696
Silver	US\$.oz	40





Why look at tin-zinc?



So why has there not been more use of tin-zinc?



Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

So why has there not been more use of tin-zinc?

- Lower electronegativity (higher electropositivity) than metals more commonly used in solders and circuitry means that zinc and alloys containing it are more susceptible to
 - Corrosion
 - Reaction with solder paste flux medium .
- 2. When zinc is in contact with more electronegative metals the electrical potential difference can drive galvanic corrosion
- 3. Even within the microstructure there are phases with significantly different electronegative potential



Why take another look at tin-zinc?



US006936219B2

(12) United States Patent Kopeliovich et al.

 (10) Patent No.:
 US 6,936,219 B2

 (45) Date of Patent:
 Aug. 30, 2005

- (54) LEAD-FREE ALLOY
- (75) Inventors: Baruch Kopeliovich, Haifa (IL); Alberto Kaufman, Haifa (IL); Yaron Man, Qiriat Tivon (IL)

(57) ABSTRACT

Lead-free Tin-Zinc alloy contains Manganese in the amount of about 0.001–0.9 wt. %. The alloy is suitable for use as a solder with commercially available fluxes. Various types of solders can be prepared from the alloy, like wire, cored wire, atomized powder, solder paste, thin sheet, ribbon foil, perform etc. The alloy has improved mechanical and electrical properties in comparison with conventional Tin-Lead alloys Sn9Zn and 63Sn37Pb.



Extract

United States Patent from: (10) Patent No.: US 6,936,219 B2

FIELD OF THE INVENTION

The present invention relates to a Lead-free Tin-Zinc alloy suitable for use as a solder. By the term "solder" here is meant a metal alloy, which when melted and applied to the joint between metal objects unites them without heating the objects to the melting point.

By virtue of the present invention the solder ensures strong and chemically stable joint between copper, brass, nickel, stainless steel and other frequently soldered metallic materials, which are used in a variety of applications including, but not limited to, electronics and general purpose soldering applications.



Extract

United States Patent from: (10) Patent No.: US 6,936,219 B2

The advantages of the solder of the invention comparing to the known in the art Zinc-containing solders are associated with the fact that the present solder does not require active & special chemistry fluxes and therefore a wide range of commercially available fluxes including VOC free fluxes can be used with the solder of the invention.

Furthermore, the solder of the invention exhibits excellent flow and wetting behavior, and therefore is very efficient in the soldering applications, where filling of tight capillary joints as well as loose ones is required.



Extract

United States Patent from: (10) Patent No.: US 6,936,219 B2

Moreover, the solder of the invention has improved corrosion resistance, since no corrosion of the substrate and oxidation of the present solder has been observed at the peripheral contact area between the solder and the substrate.

Presence of Manganese in the alloy improves its oxidation resistance and corrosion resistance and also decreases the solidification range for a relatively wide range of compositions, thus rendering the manufacturing process of the alloy more flexible.



Solder Alloys Tested

Alloy Composition	Designation
Sn + 9.1%Zn	Sn-9Zn
Sn + 7.3%Zn	Sn-7Zn
Sn + 7.1-7.2%Zn + 60-115ppmMn	SnZnMn*
Sn + 7.4%Zn + 0.5-0.6%Mn	Sn7Zn+High Mn
Sn + 3.0%Ag + 0.48%Cu	SAC305
Sn + 37Pb	PbSn

* Proprietary alloy marketed by LFSMD, Israel under the brand name "IKAlloy™"



Test	Conditions
Tensile	Bulk solder, 1 & 10mm/min
Vickers Hardness	Bulk solder, fast and slow cooled
Creep	Bulk solder, 100°C 3kg dead weight
Young's Modulus	25° C
CTE	30-180° C
Liquidus & Solidus	DSC
Ag Erosion	300°C solder bath
Electronegative Potential	Ag, Cu, Ni, Al substrates, Calomel reference electrode



Wetting Balance Test	235°C & 250°C
Chemical Resistance	17 days, 3% NaCl, 3% H ₂ SO ₄ , 3%NaOH
Heat & Humidity	85C/85%RH, 500, 1000h, Cu, Ag, Ni, brass substrates Pull test and SEM on cross sections
Ageing	150°C 500, 1000h, Cu, Ag, Ni, brass substrates Pull test and SEM on cross sections
Thermal Cycling	FR4 & CM3 substrates, -40 - +125°C, 1000 cycles
Powered Heat & Humidity	Chip resistors & capacitors, 60° C/90%RH, Cu/FR4 & Ag/glass substrates, 1000 & 2000h, measure resistance & SEM on cross sections



Microstructure

Sn-7Zn

Water Quench Interior Surface

Slow Cool Interior Surface







Primary Zn

Primary Sn





Microstructure

Water Quench Interior Su

Surface

Slow Cool Interior Surface

Sn-7.4Zn-0.006Mn



Fine homogèneous éutectic Sn-7.4Zn-High Mn SnMn₂ Intermetallic





Composition Range

- Better to keep the Zn level below the eutectic
 - To reduce the likelihood of primary Zn-rich phase in the microstructure
- Better to keep Mn below 100ppm
 - To avoid the formation of SnMn₂ intermetallic compound (550° C M.P.)



Sn9Zn





Sn7Zn





Sn7Zn0.0077Mn





Sn7Zn0.5Mn





Conclusion of DSC Studies

- Mn addition has no significant effect on solidification behaviour of Sn7Zn
- Any effect is different from that of other "X" additions like Ni or Co in SnCu or Mn or Zn in SnAgCu where there is an interaction with the intermetallics that affect undercooling behaviour.



Tensile Testing

Strain Rate 1mm/min




Tensile Testing





Tensile Testing



SnZnMn: higher UTS - lower ductility



Creep Testing



	Sn9Zn	Sn7Zn	Sn7Zn0.0077Mn
1	129.05	214.05	386.5
Ž	100.8	302.9	463.5
Ave.	114.925	258.475	425



Creep Testing



- Sn7Zn more creep resistant than Sn9Zn
- Mn further increase creep resistance



Thermal Cycling

- Connectors hand soldered with Sn9Zn, Sn7.5Zn0.26Mn, SnZnMn*
- 30 minute cycles -40° C $+80^{\circ}$ C





Thermal Cycling

Initial

1000 cycles



No significant degradation

 No significant difference

APEX Schematic Diagrams of Solder Specimens Tested

Туре	Substrates	Structure		
Hemispheric al Solder Spread Ag		Solder Surface Solder Joint Solder Joint Ni plating/Cu Substrate		
Butt Joint	Cu Brass	0.85 mm		
Peel Test	Ni Plated Cu Ag film on Glass	Ni-Plated Brass Solder 10mm Glass		

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Disks cast under conditions of

- Fast Cooling (Quench in Water)
- Slow Cooling (Air)

and exposed to heat and humidity Sn7Zn 85C/85%RH

Alloys contain zinc are more susceptible to tarnishing

Sn7Zn0.0077Mn

Sn7.4Zn0.54Mn

Tarnishing Quenched **Slow Cooled** 7 Days 7 Days Initial Initial **Exposure Exposure** Sn9Zn











SnCuNiGe

SnAgCu



SEM Images of Cross-Sections of SnZn Solders on Cu Substrates after Exposure to 85C/85%RH.



- Extent of surface corrosion of SnZnMn* was much less than that with other Sn-Zn Alloys
- A higher Mn addition is less effective in inhibiting surface corrosion.



EPMA Beam Scanning Analysis of Mn in SnZnMn* Solder Before and After Exposure to 85C/85%RH for 1000h.





FE-SEM Image and EPMA Element Maps of Cross-Section of SnZnMn* Solder on Cu Substrate After Exposure to 85C/85%RH for 1000h.



• Mn seems to be distributed homogeneously.





Effect of Mn on Sn7Zn Solders on Cu Substrate

Mn Addition	SEM	Sn	Zn	Mn
0.012 mass%	20kV X5,000 5µm 10 50 BES			
0.14 mass%	20kV X5.000 5µm 10 50 BES			
0.63 mass%	20кV X5.000 5µm 10 60 BES			

• When Mn>0.01%An Sn-Mn IMC appears to form near the interface with the Cu.

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SnZn Solders on Ag Substrate After Exposure to 85C/85%RH for 1000h



At the edge of the joint penetrating corrosion resulted in separation of the solder from substrates. Yellow arrows mark the depth of penetration.



Depth of Penetration of Solder Separation at Interface with Ag Substrates After 500h and 1000h Exposure to 885C85/85%RH



Penetration was shortest for the SnZnMn* alloy.



SnZnMn* Solder on Ag Substrate After Exposure to 85C/85%RH for 1000h.

Separation between solder and substrate









Potential Measurement Setup





Potential Measurements of Solder Alloy Reference Ag/AgCl Electrode



- $SnZnMn^* > Sn-7Zn > Sn-9Zn$
- Ranking Correlates with depth of penetration of the separation



Tensile Testing of Butt Joints





Tensile tests were conducted before and after 1000h exposure to:

- 85C/85%RH
- 150C



Preparation of Butt Joint Test Pieces





Sn9Zn/Cu Butt Joint Specimens After Tensile Testing



- As soldered and high temperature aged specimens (a), (c) failed at the solder/substrate interface.
- Specimens exposed to heat and humidity (b) failed within the solder.

Surface oxidation has a greater effect on the failure mode than galvanic corrosion.



Surface: Joint Area Ratios*

Joint Model	Exposed Surface Area	Joint Area	Surface: Joint Area ratio*
Butt Joint ^{1 mm} ^{0.85 mm} ^{1 mm} ^{2 mm} ^{51 mm}	(2*1+0.85*1)*2 =5.7 mm ²	2*0.85*2 =3.4mm ²	5.7/3.4=1.68
Peel Test Joint	(10*0.1+5*0.1)*2 =3mm ²	10*5*2 =100mm ²	3/100=0.03

* Area ratio = Surface area / Joint area



Peel Test Pieces on Ni-Plated Cu Substrate After exposure to 1000h 85C/85%RH







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Peel Test Fracture Surfaces After Exposure to 1000h 85C/85%RH for 1000h



Dark area on Sn-7Zn fracture surface Sn-7Zn>SnZnMn*.



Fracture Surfaces of Peel Test Pieces



Sn-7Zn

SnZnMn*

Fracture surfaces of Sn-7Zn solder had larger corroded area than SnZnMn*.



Fracture Surfaces of SnZnMn* Peel Test Pieces



A high level of Mn was detected inside voids associated with ZnO and halogens.



Mn-Rich Zn Compounds in Fracture Area



- Br and CI, which seem to be derived from flux, overlap exactly each other.
- Oxygen is co-located with Mn and Zn
- It is hypothesized that Mn forms MnO_x, MnCl_y, and MnBr_y, sacrificially protecting Zn from oxidation and corrosion



Peel Testing

Substrate: Fired Ag on float glass
Aging condition : 85C/85%RH for 1000h
Solder alloys : Sn-9Zn, Sn-7Zn, SnZnMn*,







Peak Peel Strength of Solder Joints on Ag on Glass Substrate



SnZnMn* on Cu Substrates Before (upper row) and After (lower row) 1000h at 150 °C



Uniform layer of CuZn IMC formed during soldering was drastically changed by counter diffusion between Sn and Cu during elevated temperature aging.

SnZnMn* on Brass Substrates Before (upper row) and After (lower row) 1000h at 150 °C.





After aging Cu-Zn IMC was $\,$ up to 30 μm thick with some evidence of cracking

Cracks in CuZn IMC

SnZnMn* on Ni-Plated Cu Substrate Before (Upper Row) and After (Lower Row) 1000h at 150°C



- NiZn IMC layer, I<1 µm thickness was formed during soldering.
- After ageing it was >10 µm thick but with a relatively smooth surface



SnZnMn* on Ag Substrates

Before (upper) and After (lower) 1000h at 150°C



Atomic%				
	Zn	Ag		
001	65.5	34.5		
002	51.6	48.4		





Silver Dissolution

Ag wires were immersed in molten solders and the remaining length of wire measured at a regular intervals.



Silver Dissolution



Erosion of Ag by SnZn solder is much less than that which occurs with SnAgCu lead-free solders and even SnPb solder.

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Dissolution of Ag Film on Glass After Soldering with Various Alloys



$\underbrace{}$

Complete dissolution of Ag substrate





Average Vertical Stresses for Hemispherical Model (N/mm²)

Property	SAC305	Sn9Zn	SnZnMn*	Sn37Pb
Linear expansion coefficient ppm 30-80 °C	23.5	22.5	22.3	25.5
Linear expansion coefficient ppm 80-130°C	24.3	23.3	23.5	28.5
Linear expansion coefficient ppm 130- 180°C	25.4	24.3	25.5	28.0
Young's modulus Gpa	50.8	56.9	50.0	41.2
Melting Point (°C)	217	198	198	183
Average vertical stress N / (mm) ²	8.35	8.12	7.29	5.83
Stress ratio	1.43	1.39	1.25	1



Hemispherical Model of Solder Joint

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Estimated Average Vertical Stress on Solder/Glass Interface



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Young's Modulus

Test Method: JIS R1602 Young's modulus, Resonance method Poisson's ratio: Calculted using the following formula use:

v = E/(2G) - 1

Solder Alloy	Poisson's ratio	Shear modulus(GPa)	Young's modulus (GPa)
SnCuNiGe	0.41	18.8	53.2
Sn7Zn0.0077Mn	0.36	18.4	50.0
Sn9Zn	0.38	20.6	56.9

SnZnMn* alloy has relatively low Elastic Modulus



Coefficients of Thermal Expansion

Instrument: TD5000S (Mac Science) Sample: 5-6mm diameter, 16-17mm length Standard: 5mm diameter, 17mm length







Coefficients of Thermal Expansion

	Coefficient of Thermal Expansion (ppm)						
()	SnCuNi Sn9Zn Sn7Zn Sn7Zn0.007Mn Sn7Zn0.003Mn Sn3Ag0.5Cu Sn3						Sn37Pb
30-80	24.3	22.5	22.0	22.3	23.1	26.5	25.5
80-130	25.4	23.2	23.5	23.5	24.1	27.2	28.5
130-180	26.5	24.3	24.2	25.5	26.3	26.7	28.0





Basis for Stress Modelling



Properties

	Linear expansion coefficient	Young's modulus	Poisson's ratio
Solder	$lpha_{\scriptscriptstyle S}$	E_{S}	${\cal V}_S$
Glass	$\alpha_{_G}$	E_{G}	V_{G}

Lengths

	X Direction	Y direction	Z direction
Solder	l_{Sx}	l_{Sy}	l_{Sz}
Glass	l_{Gx}	l_{Gy}	l_{Gz}

Cross-sections

	X Direction	Y Direction	Z Direction
Solder	A_{Sx}	A_{Sy}	A_{Sz}
Glass	A _{Gx}	A_{Gy}	A_{Gz}

APEX FOR Estimating Stress Generated During Cooling from Solidus

Property	SnPb	Sn3.0Ag0.5Cu	Sn0.7Cu0.05Ni+Ge	Sn7.4Mn<0.01Mn	Sn9Zn
Linear expansion coefficient ppm 30-80 °C	25.5	26.5	24.4	22.3	22.5
Linear expansion coefficient ppm 80-130°C	28.5	27.2	25.4	23.5	23.3
Linear expansion coefficient ppm 130-180°C	28.0	26.7	26.5	25.5	24.3
Stress in the elastic region * N / (mm) 2	766.1	3179.9	887.5	713.3	869.4
Melting Point (°C)	183	217	227	198	198
Shrinkage ΔL in the freezing point °C 20 \rightarrow / Liquidus	0.00444	0.00527	0.00530	0.00425	0.0041 7
Stress N / (mm) ²	3.4	16.8	4.7	3.0	3.6
Stress ratio	1	4.93	1.38	0.89	1.07





Effect of CTE difference and Elastic Modulus

Thermal Cycling





Heat Shock: -40° C - +90° C, 90min/cycle On Ag/Glass

	Cracks			
	30 cycles	60 cycles		
SnCuNiGe	0/5	0/5		
SnAgCu	0/5	1/5		
Sn9Zn	1/5	3/5		
SnZnMn*	0/5	0/5		





Activation System Proposed for Flux Medium for SnZnMn* Solder Paste





Shelf life of SnZnMn* paste with Flux Medium with "Blocked" Activation System







Wetting Behavior

Solder pastes made up with a flux medium specially formulated for compatibility with zinc-containing solder. Preheat 160° C and Reflow 120 seconds at 230° C

	Copper	Brass	Nickel	
SnZnMn*				
Sn9Zn				
SnZnAl				



Typical Reflow Soldered Joints

SnZnMn





Conclusions

Corrosion Inhibition

- The addition of <0.1% Mn to a near eutectic Sn-Zn solder:
 - Significantly reduced the extent of surface corrosion of SnZn in 85C/85%RH
 - Significantly reduced penetration of galvanic corrosion at the interface with a Cu substrate
- The reduced corrosion appeared to correlated with a reduction in the apparent electronegative potential of the Sn-Zn alloy



Conclusions (continued)

Inhibition Mechanism

- The Mn appears initially to be homogeneously distributed within the solder
- The concentration of Mn in the corrosion products after exposure to heat and humidity suggests it protects the alloy sacrificially.



Conclusions (continued)

Interfacial Reactions

- The interfacial IMC formed on Cu and brass substrates grows rapidly during elevated temperature ageing and develops cracks
- The interfacial IMC formed on NI and Ag is relatively stable in elevated temperature ageing



Conclusions (continued)

Substrate Dissolution

 Near eutectic Sn-Zn solder dissolves Ag substrates much more slowly than conventional Sn-Cu and Sn-Ag-Cu Pb-free solders and even Sn-Pb solder.

Substrate Stress

 Because of relatively low CTE and Elastic Modulus near eutectic Sn-Zn solder imposes lower stress on the substrate that conventional Sn-Cu and Sn-Ag-Cu Pb-free solders



SUMMARY

- The use of microalloying additions such as Mn might make it possible to find some application for alloys based around the Sn-Zn eutectic.
- There is much more work to do!

Thank You

your partner for soldering solution

