BALVER ZINN®
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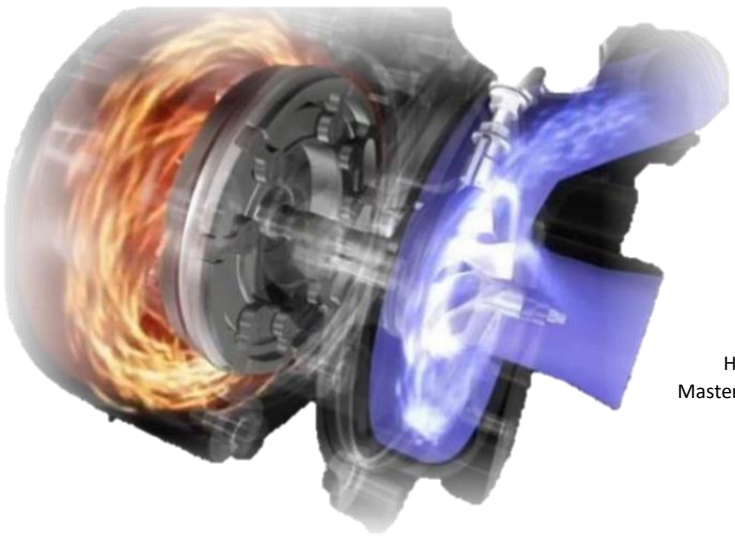
2018

BALVER ZINN ®

SN100CV® - Setting New Standards

To ensure long-term reliability of lead-free solders under harsh environmental conditions

SN100CV® exploits the Bi-effect to ensure long-term reliability of electronic devices under harsh environmental conditions through an ingenious alloying mechanism.



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1. Introduction

Since the introduction of EU directive 2002/95/EG, lead free soldering processes have become a commodity and are widely implemented in electronics assembly. For some dedicated high reliability products such as automotive, military, aerospace and medical applications, lead containing alloy is still allowed although over time the number of these exemptions will be reduced.
For high temperature applications currently available lead free solder alloys might exhibit limitations in reliability.

1.1 Harsh Environment for Electronic Devices

Electronic devices that are exposed to high operating temperatures as in the internal combustion engine and power train applications require improved characteristics to meet these harsh environment conditions. In addition to high temperature, sensors and controllers in automotive applications are subjected to harsh vibrations and other mechanical stresses. Such products should be manufactured with this in mind.

1.2 Ageing mechanisms in solder joints.

Besides mechanical stress, solder joints can be subjected to thermal stress due to continually changing temperature. This thermal stress may lead to fatigue fractures in the alloy eventually resulting in a broken solder connection.
Because of differences in CTE (Coefficient of Thermal Extension) of the various component materials changes in temperatures will lead to inner metallic stresses. At the same time this thermal impact promotes a coarsening effect (growing of the metallic phases) in the solder which will make the alloy more brittle.

2. Strengthening mechanisms in solder systems

A lead-free solder connection consists of a tin matrix with different phases governed by alloy and component material, for example Ag_3Sn, Cu_6Sn_5, $(CuNi)_6Sn_5$ or other phases. The number and amount of the different phases increases if the alloy system has a more complex structure. Their formation leads to solidification of a very soft tin matrix.

Two of the most frequently used solidification mechanisms in soft soldering systems, precipitation strengthening and solid solution strengthening (substitution consolidation), will be now explained further.

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2.1 Precipitation strengthening

Precipitation strengthening is based on the formation of intermetallic phases such as Cu_6Sn_3 and Ag_3Sn in the solder. They are formed during the soldering process that connects the component to the printed circuit board, and are evenly distributed in the joint structure.

Due to the thermal load of temperature ageing or temperature cycling of electronic assemblies in service, intermetallic phases coarsen and create a rough micro structure. This process is dependent on the number of thermal cycles, the temperature and the time at temperature. Long periods at high temperature confer rapid growth of grain structure and intermetallic which leads to embrittlement and degradation of the solder joint. Therefore, precipitation strengthening has limited thermal stability.

2.2 Solid solution strengthening

Another strengthening mechanism for the soft tin matrix is to disturb the regular crystal structure of the Sn-crystals by incorporation of "foreign atoms".

By choosing alloying elements with a larger atomic radius than Sn, the tension in the tin matrix (which equates to strength) between the Sn atoms will be reinforced.

The exchange of Sn atoms with foreign atoms (e.g. Bi) in the crystalline structure is called substitution.

Incorporating foreign atoms prevents dislocation of the Sn atoms in the matrix under load and as such results in a strengthening of the system. Solid solution strengthening is independent of intermetallic phase growth and the associated coarsening effect and leads to a solder connection with greater thermally stability.

3. Systems and challenges

Binary alloys like Sn63Pb37 with a relatively low melting temperature of 183° C will no longer fulfil many customer requirements due to increased thermal demands in electronic assembly devices. Current high reliability alloys, for example the well-known SAC305 alloy with 3% of Ag and 0.5% of Cu, contain at least 3 elements.

To achieve some specific high reliability characteristics other solder compositions contain up to 6 elements. However, although these special alloys have some advantages, production processes are more sensitive due to increased complexity.

3.1 Alloy Stability

Making solder interconnections in electronics assembly can be achieved by reflow, wave, selective, robot or manual soldering processes.

These processes require delivery of different alloy formats that may influence final composition, especially when the alloy is molten for a long period as in wave and selective soldering: does the alloy fractionate? Is there intermetallic formation that accumulates in specific areas of the solder bath? Variations in the thermal mass of components, heat sink effects and different cooling gradients may influence final alloy composition: is the composition of each individual solder joint in an assembly homogeneous and does it fulfil specifications?

3.2 Delivery format, pricing and resources

To make production processes cost effective with a uniform solder system, various delivery formats and sizes should be available. Solder powder as used in solder paste with particle sizes in the range of 5-15µm (IPC Type 6) and flux cored solder wire with diameters down to 0.3 mm or smaller should be offered alongside bar solder and solid wire while retaining cost effectiveness.

It should be taken in consideration that some elements in the alloy can influence oxidation rate which is important when handling solder paste. Also the ability to produce flux cored solder wires may have limitations and should be taken into consideration.

Expensive elements like silver and indium are often used to achieve high reliability. Although these are only present in small amounts, they will exert a large effect on the final price of the alloy. The long term availability of all alloy components should always be considered: the best solder is that one that is available!

4. SN100CV® - The bismuth effect

SN100CV® is a Nihon Superior patented alloy for high-end applications with a unique combination of 3 soldering systems creating the ideal compromise between high-end reliability and economic efficiency.

SN100CV® combines a silver-free soldering system with bismuth and micro-doped nickel and germanium. The bismuth is reinforcing the tin matrix through the substitution principle increasing the strength by approximately 30% compared to standard SN100C® alloys, meeting or even exceeding those of standard SAC305 (SnAg3Cu0.5) alloys.

4.1 Physical properties, characteristics and composition

Based on the eutectic solder composition SnCu0.7Ni0.05Ge0.005 the trademark SN100C® has received an upgrade of 1.5% bismuth and is released under the registered name SN100CV®.

Due to this addition of 1.5% bismuth the melting point of SN100C® is reduced from the eutectic 227°C to a melting range between 221°C and 225°C. SN100CV® will be available in all formats such as solder paste, flux cored solder wire, solid solder wire and different shapes of solder bar in order to service all available soldering processes.

ITEM	SN100C	SN100CV	SAC305	TEST METHOD
Solidus (°C)	227	221	217	Differential scanning calorimetry: Temperature ramp rate: 2°C/min Measurement range 30-300°C; JISZ3198-1
Liquidus (°C)	227	225	219	
Specific gravity (g/cm³)	7.4	7.4	7.4	Archimedes method Weight of water displaced
Tensile strength (Mpa)	32	52	48	Strain rate 10mm/min Test temperature:25°C
Elongation (%)	48	33	33	Strain rate 10mm/min Test temperature:25°C
0.2%Proof stress (MPa	n.a.	39	41	Strain rate 10mm/min Test temperature:25°C
Young's modulus (GPa)	n.a.	55	51	Free resonance method
Linear expansion coefficient (ppm/k)	n.a.	24	23	Differential expansion method
Thermal conductivity (W/m·k)	64*	54	58	Laser flash method
Specific heat (J/(kg·K))	220*	224	219	Laser flash method
Electrical resistivity (μΩm)	0.13	0.14	0.14	Four-terminal method
*	Estimated Value			
n.a.	Not Available			

Tab. 1: Properties of SN100CV® compared to SN100C®and SAC305

4.2 The optimal bismuth content

A correct bismuth content in the tin matrix is crucial for solder joint reliability over the entire operational temperature range. At room temperature only a very small amount of bismuth can be dissolved. Bismuth content outside of the solubility limits (Fig. 1) should be avoided as this will precipitate below the solubility temperature.

For example, a bismuth content of about 6% by mass at a temperature above about 60°C is completely dissolved in the tin matrix. When the solder is cooled to room temperature, the bismuth begins to precipitate (Fig. 2).

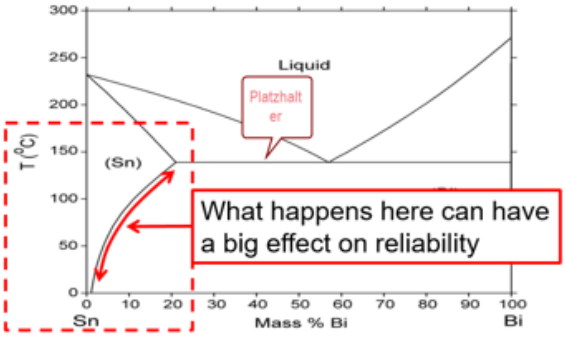

Fig. 1: The correct amount of bismuth in the tin based lead free solder alloy is critical to the reliability of the solder joint

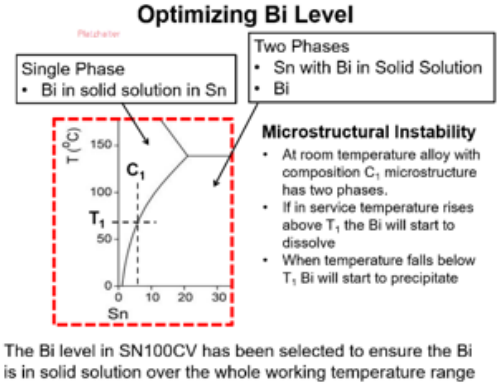

Fig. 2: The right mixing ratio of alloy components is also important, because surplus bismuth precipitates at room temperature

If bismuth content is higher than the solubility limit at a specified temperature, this can lead to microstructural instability of the alloy. In such cases the solder structure might consist of two different phases, SnBi crystals and precipitated bismuth.

Bismuth that goes into solution at soldering temperature may precipitate once the assembly has cooled to below the solubility limit. This can be considered as a critical phenomenon that influences the reliability of the final solder joint.

SN100CV® contains a non-critical bismuth content of 1.5% to avoid this precipitation phenomenon and as such can ensure complete solubility of the bismuth in the alloy at all temperatures.

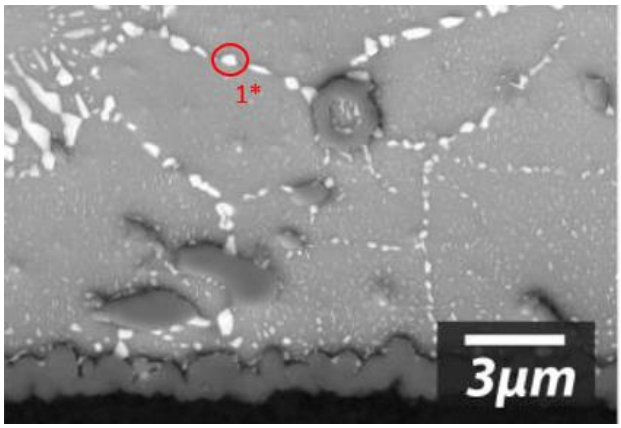

Fig. 3: If the bismuth content is too high, then a Bi-phase forms in inter-dendritic areas

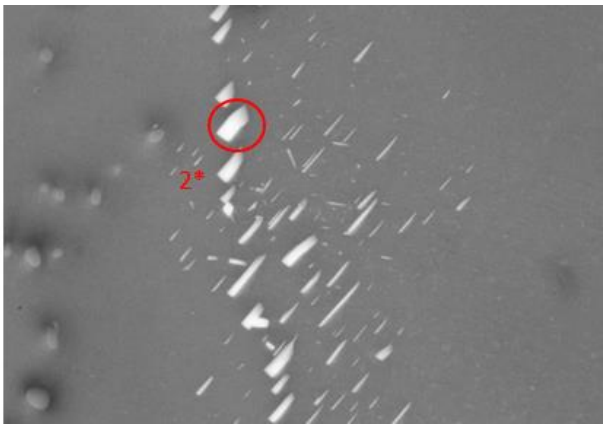

Fig. 4: Bi-phases separating on Sn-crystals

4.3 Reliability and thermal stability

In SN100CV® bismuth increases the strength of the solder. Solid solution hardening causes "interlocking and distortion" of the metal grid during solidification making SN100CV® thermally very stable. In term of tensile strength, yield strength and shear strength SN100CV® meets or even exceeds values for standard silver containing alloys like SAC305.

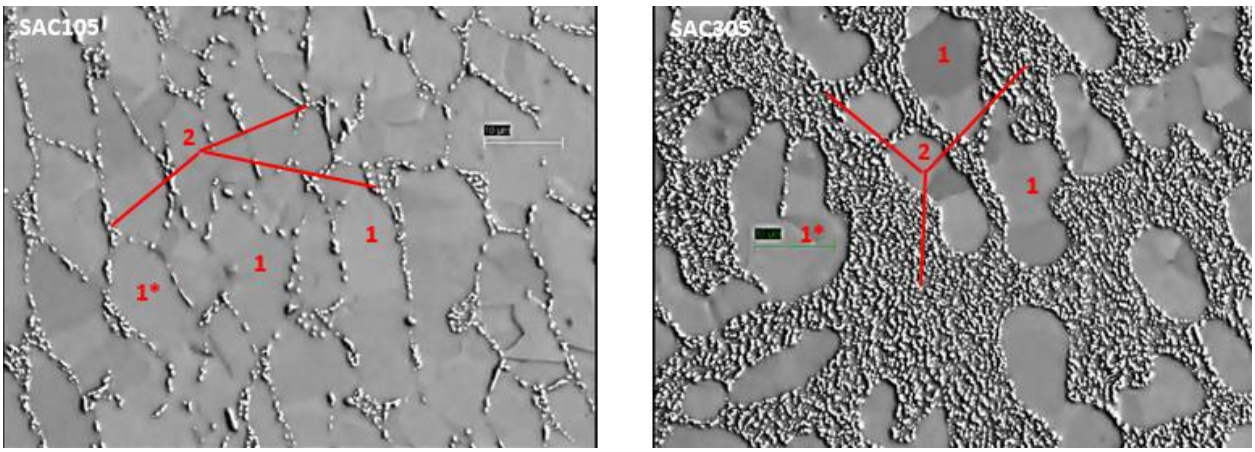

Fig. 5: *1 shows prime Sn-dendrites in SAC105 and SAC305 after soldering. 2 shows Sn+Ag_3Sn+Cu_6Sn_5 eutectics after soldering

Therefore, the thermal stability of SN100CV® is not significantly affected by precipitation strengthening in which the rapid growth of the intermetallic phases can lead to embrittlement.

By contrast, ageing alloys containing different concentrations of silver for 2520 hours at 125°C demonstrates the limits of precipitation hardening due to the “Oswald Ripening”. During this process, the Ag_3Sn particles grow and coarsen the structure of the solder.

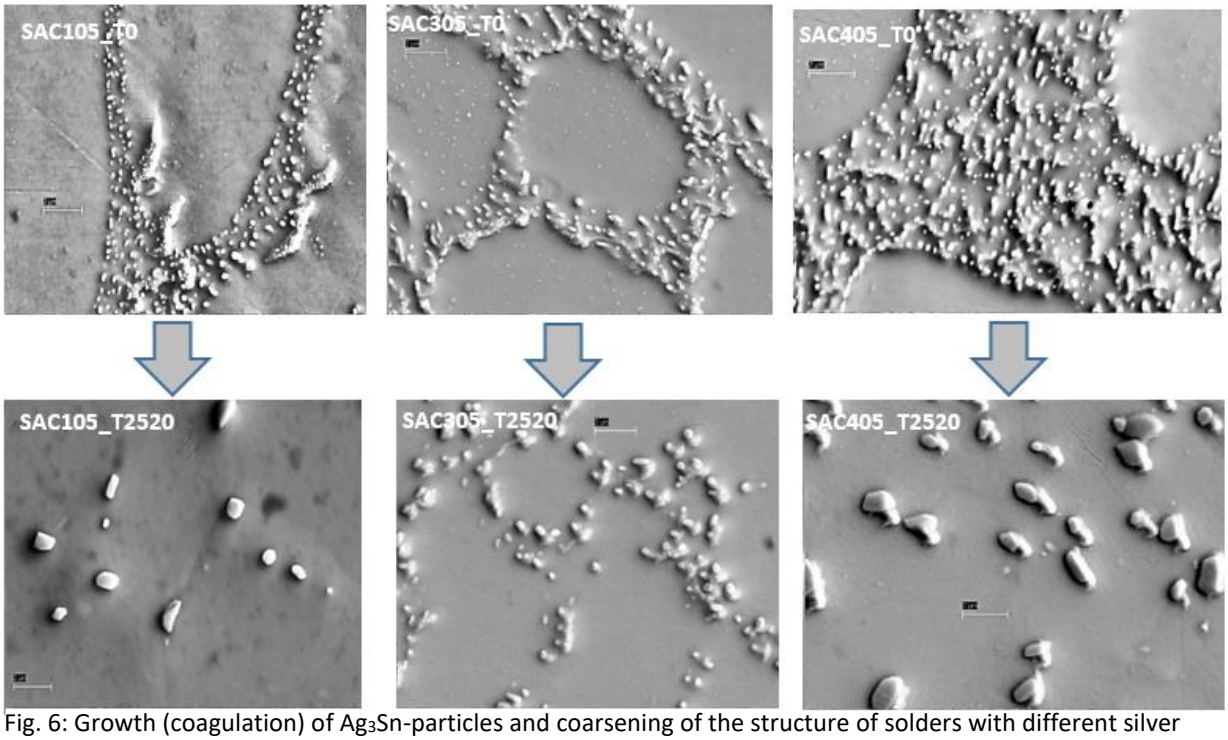

Fig. 6: Growth (coagulation) of Ag_3Sn-particles and coarsening of the structure of solders with different silver contents after 2.520 hours at 125°C

4.4 Weibull-analysis, the approved method to evaluate reliability

Weibull analysis is often used in conjunction with electronic assembly life time and failure probability evaluations. Weibull distribution describes the probability of failure in electronic assemblies, taking into account history of ageing under real or simulated conditions.

4.5 Components and metallization of printed circuit boards

Another factors that influence long term reliability of the solder joint are component type and metallizations of the component lead and substrate.

To illustrate this copper and ENIG finished substrates were exposed to standard and micro-doped alloys. The influence of the component was investigated with SMT components of the types DRMLF156, MLF100 and BGA360.

Compared to other alloys SN100CV® shows the lowest sensitivity to PCB metallization after thermal cycling. This can be explained by the micro-addition of nickel that stabilizes the hexagonal crystalline structure of the Cu76Sn5 IMC phase. Solder that does not have micro-doped Ni in their specification cannot benefit from this stabilization effect which is most obvious with IMC on Cu.

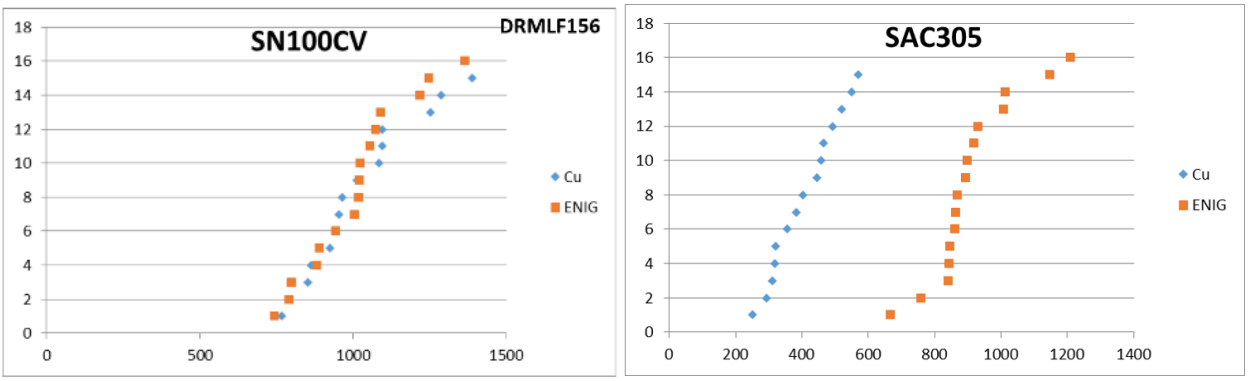

Fig. 7: Lower sensitivity (interaction) with SN100CV® compared to SAC305

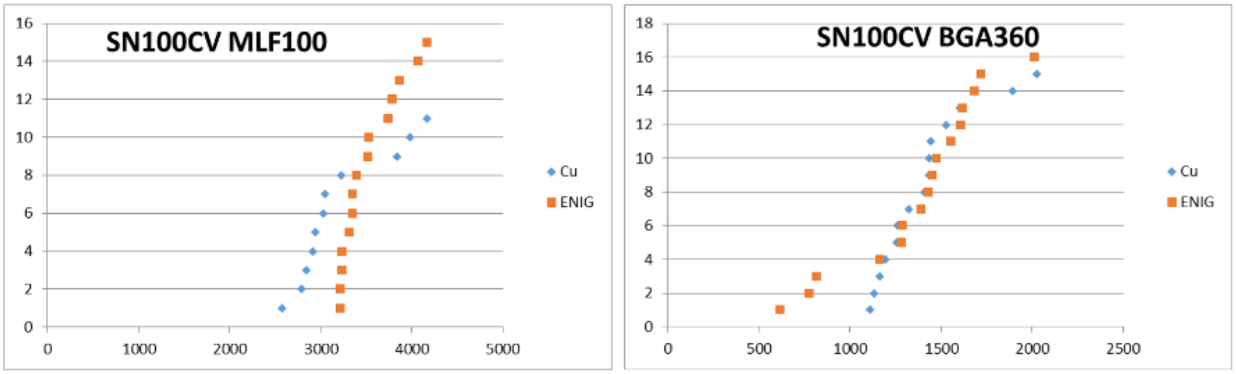

Fig. 8: Low sensitivity of SN100CV® even on components with other housing types

4.6 Shear resistance and thermal stability

The experimental setup for simulating creep strength consists of loading specimens at 125°C with two different weights (100 kg and 120 kg).

Fig. 9: Creep resistance at 125°C and 100kg /120kg. Faster creep with SAC305 as Ag_3Sn particles coarsen the alloy

To assess isothermal shear resistance, the solders (assemblies) are examined and compared under constant conditions 125°C.

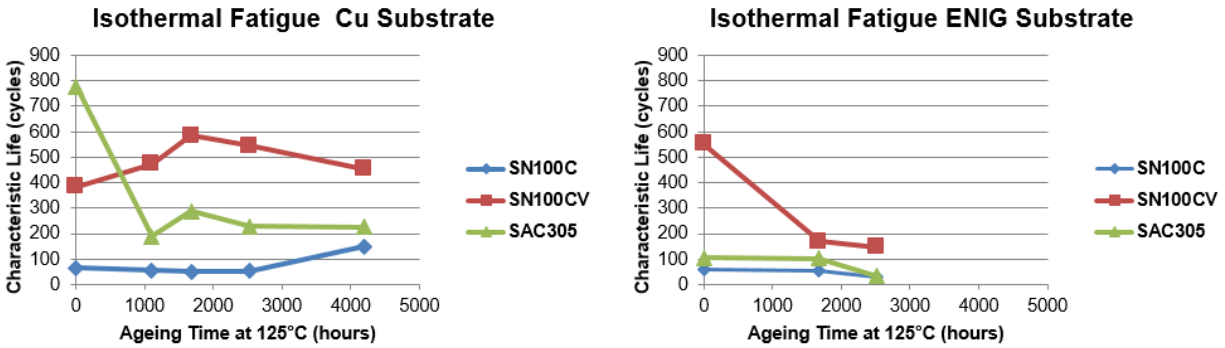

Fig. 10: Reduction of characteristic lifetime due to solder joint ageing

Due to the previously described strengthening and ageing mechanisms, SN100CV® shows a significant increase in strength and better thermal stability than SAC305.

5. SN100CV® - Results of accelerated ageing

In addition to shear- and creep resistance, a temperature shock test (-40 / + 125 °C, 15 min.) has been conducted to further evaluate characteristics and to simulate solder joint ageing.

From the start SN100CV® shows equal or partially better rigidity values compared to SAC305, which is confirmed in similar form even after 1000 or 2000 temperature cycles.

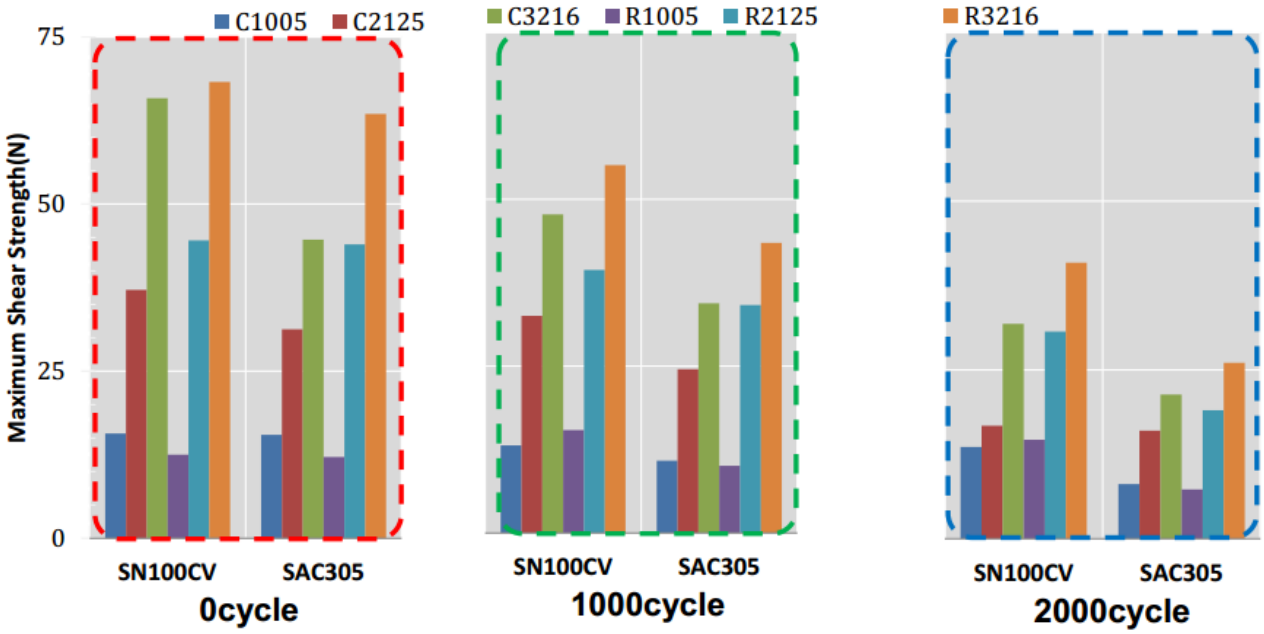

Fig. 11: Maximum shearing force for SN100CV® and SAC305 after temperature cycling across different component sizes

Micro-sections after 0, 500, 1000 and 2000 cycles show the fine-grained structure of SN100CV®. Damage of the solder joints due to ageing can be detected both in SN100CV® and, even more pronounced, in SAC305, especially after 2000 cycles.

By adding bismuth, it has been possible to bring the outstanding characteristics of SN100CV® to the level of silver containing and thus highly priced solders such as SAC305, and in some cases outperform them.

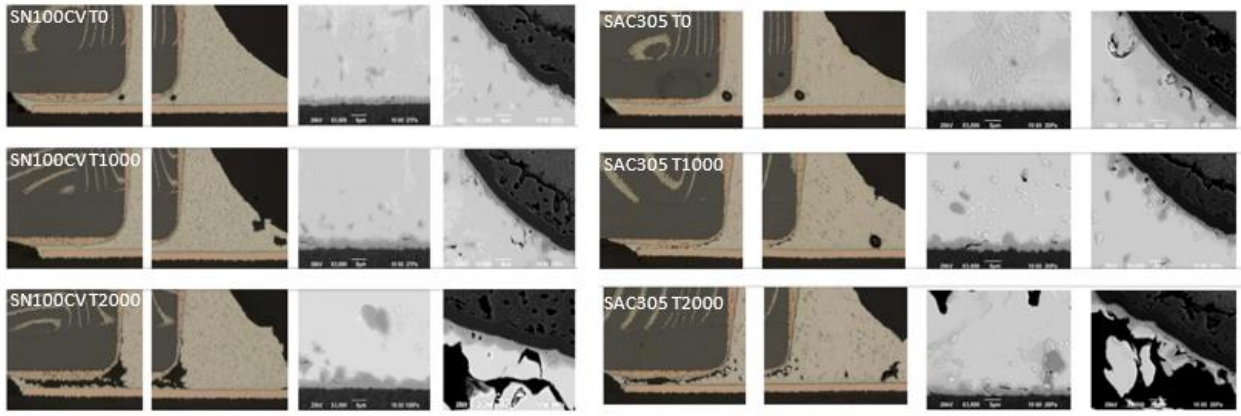

Fig. 12: Micro-section of solder joints with SN100CV® or SAC305 after temperature cycling

5.1 Preliminary conclusion

It seems that SN100CV® only has advantages when compared with SAC305, and in fact there are hardly any disadvantages. Nevertheless, there is a fundamental question for the process technologist: with which reflow profile should a solder system with 221 - 225 ° C melting temperature be processed, as the liquidus temperature is 6 ° C higher than that of SAC305?

To answer this, assemblies were processed at Tpeak = 225, 230, 235 and 240°C. After soldering visual and micro-section inspection was conducted. In contrast to SAC305, reflow profiles with 225 °C peak temperature are not expected to melt SN100CV® solder paste. However, tests clearly showed that an optimally adjusted reflow profile with Tpeak=230 ° C forms a very good solder meniscus and has good wetting. Therefore, with today's peak temperatures of 235 - 240 °C, most modules are easily processed.

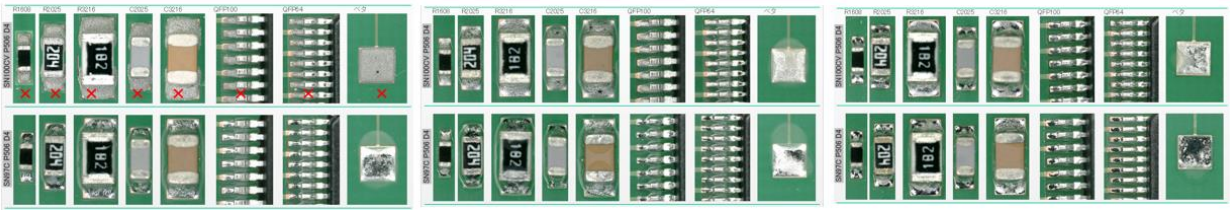

Fig. 13: Comparison of SAC305 and SN100CV® at peak temperatures 225°C, 230°C and 240°C

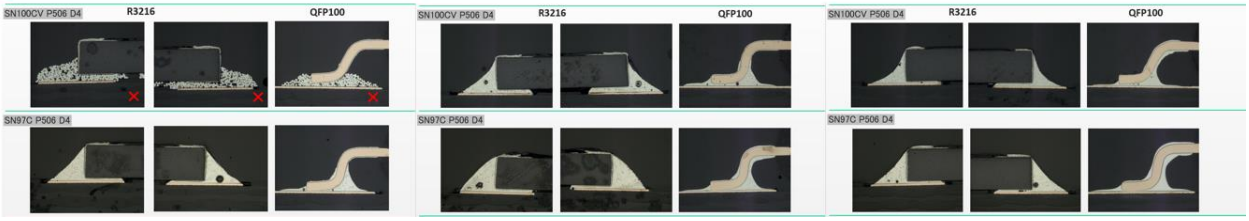

Fig. 14: Micro-section comparison of SN100CV® and SAC305 at peak temperatures 225°C, 230°C and 240°C

6. Summary

Following the introduction of Pb-free technology Balver Zinn presented silver free SN100C® alloy to the market. Currently this is the most popular alloy in soldering processes and is standardized as Alloy 403 according DIN EN ISO 9453:2014-12.

As processes and materials have become standards, new challenges have to be faced, for example device miniaturization and associated implications for solder powder, stencils etc. Also we have seen a tendency of Low Melting Point Alloys suitable for some consumer applications. Another challenge is the continuous search for high reliability alloys for harsh environment applications.

Balver Zinn has reacted to the challenge of high reliability in harsh environment by presenting SN100CV® alloy.

SN100CV® is a cost effective solution for the electronics assembly industry that will serve 80 to 90% of the total market. It has proven to be a very reliable alloy compared to SAC305 and will offer a huge cost saving because of the absence of silver in the alloy.

SN100CV® is available in all common delivery forms like bar and solid wire for wave and selective soldering, solder paste for reflow applications and cored wire for touch up and manual/robotic soldering.

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