Drop Shock Reliability of Lead-Free Alloys – Effect of Micro-Additives

Ranjit S Pandher, Brian G Lewis, Raghasudha Vangaveti, Bawa Singh
Cookson Electronics, Assembly Materials Group
600 Route 440, Jersey City, NJ 07304, USA
Email: rpandher@cooksonelectronics.com

Abstract

The drop shock reliability of solder joints has become a major issue for the electronic industry partly because of the ever increasing popularity of portable electronics and partly due the transition to lead free solders. Most of the commonly recommended lead-free are high Sn alloys which have relatively higher strength and modulus. This plays a critical role in the reliability of Pb-free solder joints. Further, even though metallugically it is the Sn in the solder alloys that principally participates in the solder joint formation, details of the IMC layers formed with SnPb and Pb-free alloys are different. The markedly different process conditions for SnPb and Pb-free alloys also bear on solder joint quality.

Brittle failure of solder joints in drop shock occurs at or in the interfacial IMC layer(s). This is due to the inherent brittle nature of the IMC, defects within or at IMC interfaces or transfer of stress to the interfaces as a result of the low ductility of the bulk solder.

In developing improved performance alloys, Cookson Electronics has addressed both issues – improved ductility and modification and control of the intermetallic layer. A broad range of base alloy compositions together with selected micro-alloying additions to SnAgCu alloys have been evaluated with the objective of controlling bulk alloy mechanical properties and the diffusion processes operating in the formation and growth of the intermetallic interfacial layer(s).

In the present article a detailed study of a range of micro-alloy additives is presented. The alloy additives generally act as diffusion modifiers slowing interdiffusion between substrates and solder thereby reducing IMC thickness or the propensity for void formation. Alternatively additions can be made that act as diffusion compensators©. It should be noted that the level of the micro-additions does not measurably modify the bulk mechanical properties of the base alloys. Our results show that dramatic improvements in the solder joint reliability, as demonstrated by high-speed ball pull and drop shock tests, can be achieved.

Introduction

With the electronics industry move to Pb-free soldering, SAC305 and SAC 405 became the alloys of choice based on lowest available melting temperature, near eutectic composition and acceptable to good cyclic fatigue properties. There were early suspicions that, while SAC 305 or SAC405 clearly met many of the specifications for a successful Pb-free solder, as the database of properties grew there would be performance gaps. That has proven to be the case. Concurrent with the world wide Pb-free alloy initiative we have seen the proliferation of portable electronics. These devices have highlighted the need for good drop shock reliability and it is in this arena that SAC305 and other relatively high Ag SAC alloys have significant shortfalls.

The root cause of the poor high strain rate response of SAC305 like alloys relative to eutectic SnPb lies in the bulk alloy properties. Most Pb-free solders are high Sn alloys with up to 5%Ag and 1% Cu. These alloys have a relatively higher strength and modulus and lower acoustic impedance and therefore under conditions of drop shock more readily transfer stress to the solder-substrate interface. The intermetallic compounds (IMC) formed during soldering are of low ductility and it is this interface that exhibits brittle failure in test.

A large number of alloys have been evaluated and discussed in the literature as alternatives to high Ag SAC alloys for BGA and CSP dependent devices. The first factor addressed is bulk alloy properties. The effect of the higher strength of high Sn alloys can be minimized through the selection of low Ag alloys. At lower Ag there is less Ag_3Sn IMC in the bulk alloy with concomitant reduction in mechanical strength. The shear strength for the SAC family of alloys is shown in Figure 1. Clearly lower Ag alloys have an advantage in potentially absorbing the effect of high strain rate deformation.

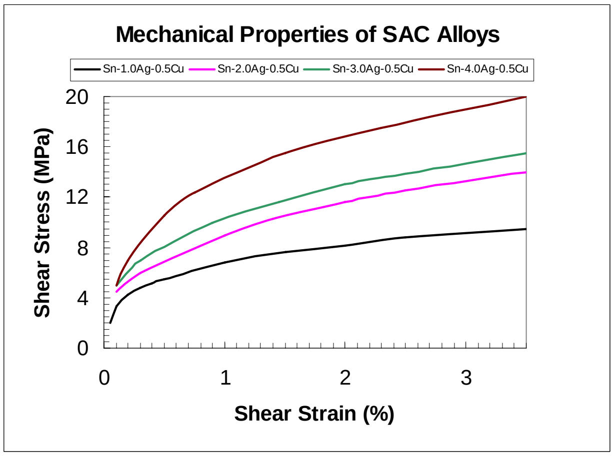


FIGURE 1: Mechanical (shear) properties of SAC alloys as a function of Ag content. Data is from Ref. [1]

The second factor examined is the nature and amount of the IMC formed in soldering. This is a complex area. High strain rate brittle fracture can be encountered in soldering with Pb-free solder to all electronic substrates including OSP Cu, ENIG, matte Ni and sputtered Au/Ni. The interfacial IMC formed is determined by the phase equilibria (free energies) of the high Sn solder and the substrate, so that, for example, in soldering to Cu with a SAC alloy Cu_6Sn_5 is the equilibrium phase at the Sn rich solder interface while Cu_3Sn is in equilibrium with the substrate. The quantity of IMC formed is a function of soldering time and temperature and subsequent aging conditions. The degree to which a particular soldered interface is susceptible to brittle failure depends on the composition of the IMC e. g. Cu_3Sn is the more brittle of the two binary CuSn IMCs, the thickness of the IMC and the presence of defects either as (Kirkendall) voids, incipient cracks or residual stress between IMC layers e. g. $(Ni,Cu)_6Sn_5$ over $(Ni,Cu)_3Sn_4$ [2,3]. Improved drop shock performance can be improved therefore by controlling the initial IMC formation, its subsequent development through device life and the IMC defects.

In developing improved performance solders, Cookson Electronics has addressed ductility through the development of low Ag SAC alloys with improved wetting and spread properties and modification and control of IMC through manipulation and combinations of micro-alloying additions.

In this paper we compare the performance of the SAC alloy family with Cookson proprietary SACX alloys with and without micro-alloying additions. The role of Ag and Cu in SAC alloys is a straightforward issue of Cu_6Sn_5 and Ag_3Sn strengthening of the Sn matrix. Reducing the Ag content while maintaining a Cu level to manage substrate dissolution and with the addition of Bi to improve wetting and fatigue properties [4] has provided an alloy platform for the development of micro-additions.

The role of micro-alloying additions in modifying the IMC development is specific to the addition and has been discussed by various authors. Andersen et al [5] has discussed improvements in the brittle failure of SAC alloys with the addition of Co and Fe in terms of slowing the diffusion of Cu from the substrate. This minimizes the formation of the brittle Cu_3Sn phase and also serves to reduce the propensity for void formation. Gao et al [6] discuss a similar reactive diffusion situation with Co and Ni additions in terms of thermodynamic models and conclude that Co and Ni have a greater affinity for Sn than Cu and their partition may be expected to nucleate Cu_6Sn_5 at the expense of the nucleation and growth of Cu_3Sn. In the absence of the transition metal additive grain boundary diffusion can lead to significant IMC growth. The degree to which a small Ni addition can inhibit Cu_3Sn growth is shown in Figure 2.

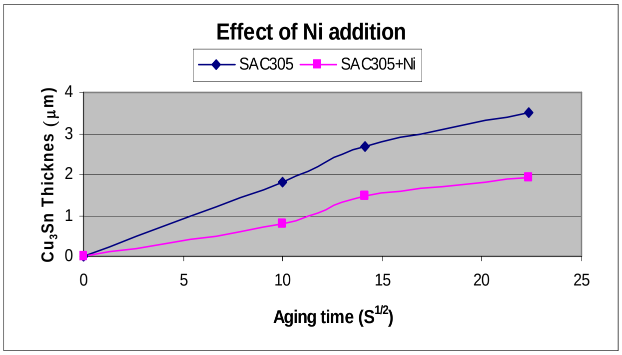


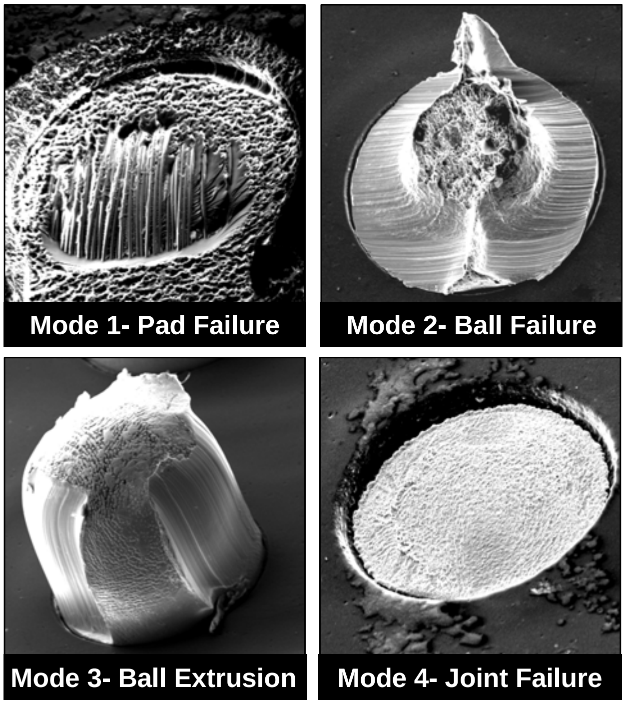
FIGURE 2: Intermetallic growth of SAC305 and SAC305 + 0.1% Ni soldered to OSP Cu

In parallel work Cookson has developed a range of low melting Pb-free alloys based on SnZn [7]. In these alloys micro-alloying with In, Ni, Fe and Co has been effective in modifying the eutectic composition to lower Zn content for improved corrosion resistance and providing highly mobile diffusing species e. g. In, that act as diffusion “compensators” © and minimize Kirkendall porosity in SnZn – Cu solder joints.

The work presented below details the high strain rate behavior of low Ag SAC alloys with combinations of Bi, Ni, Cr, Ge and In additions. The micro-additions were chosen to optimize the bulk alloy properties, to modify IMC development and to improve the oxidation behavior of the solder alloy.

Experimental Procedures

The experimental work was conducted on Dage 4000 and Dage 4000 HS Ball Pull and Ball Shear systems. The Dage 4000 machine is capable of performing ball pull test at speeds up to 15 mm/sec while the Dage 4000 HS can do the same test up to 1000 mm/sec. All the tests were carried out using 18 mil (450 μm) spheres assembled on CABGA100 substrates and 12 mil (300 μm) spheres assembled on CBGA84 substrates with NiAu pad finish. Spheres were assembled using a water soluble paste flux (Alpha WS9180-M3) that was stencil printed on the substrates. Spheres were placed using a simple manual alignment assembly setup and reflowed in air, in a seven-zone convection reflow oven. Two low silver SnAgCu base alloys (SAC105: Sn1.0Ag0.5Cu and SACX: Sn0.3Ag0.7Cu0.1Bi) along with common SAC alloys SAC405 and SAC305 for reference were used with a range of micro-additives. Failed samples were categorized by failure mode, as shown in Figure 3 for ball pull.


Mode 1- Pad Failure

Mode 2- Ball Failure

Mode 3- Ball Extrusion

Mode 4- Joint Failure

FIGURE 3: SEM pictures of ball pull failure modes

Mode 1 – Pad failure:

The whole pad comes off the substrate indicative of a board or substrate quality problem.

Mode 2 – Ball Failure / Neck Break:

Failure occurs in the bulk of the solder material indicative of a ductile failure. This is the preferred failure mode.

Mode 3 – Ball Extrusion:

This occurs because of improper placement of the pull tool or a solder that is too soft.

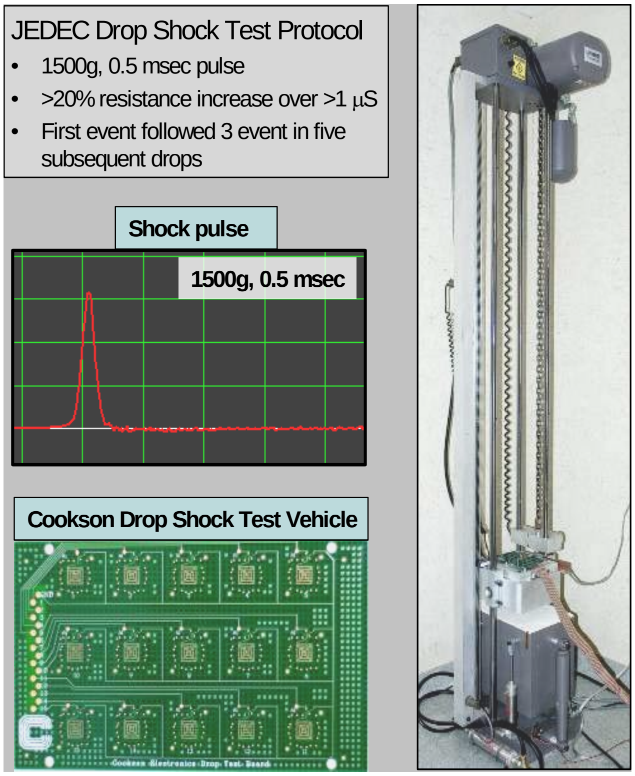
Mode 4 – Joint failure /IMC failure:

Failure occurs at the solder pad interface. This failure may have a larger peak force and is predominantly a brittle failure.

High Strain Rate Metrology

JEDEC JESD22-B111 procedure for drop shock is the definitive test method used to evaluate portable electronics [8]. It is however a lengthy and expensive test to run. For BGAs and CSPs, ball pull and ball shear can be used to evaluate solder sphere performance. We have shown that high shear rate and high speed ball pull using the DAGE 4000HS emulate drop shock performance [9, 10]. Further, following high temperature (150°C) aging and the growth of IMC phases, standard ball pull and shear using a DAGE 4000 can reproduce drop shock results.

We report here a combination of high speed ball pull and drop shock tests using a Lansmont Drop Shock tower (Figure 4) on CABGA100 assemblies.



JEDEC Drop Shock Test Protocol

- 1500g, 0.5 msec pulse
- >20% resistance increase over >1 µS
- First event followed 3 event in five subsequent drops

FIGURE 4: Drop shock system and JEDEC test protocol

In addition to high strain rate tests like high-speed ball pull and drop shock, alloys' wetting/spread behavior was also investigated. 12 mil spheres were placed on stencil printed flux on Cu-OSP coupons and reflowed in a seven zone convection oven in air. OSP coupons were used as the poor wetting on OSP is more discriminatory. After reflow the coupons were cleaned in hot water to remove any flux residue. During reflow the solder wets the surface and spreads around. The area of the wetted surface is measured and the spread factor is determined as the fractional increase in area relative to the projected cross-section of the sphere.

Results

In Cookson Electronics' alloy development program, a broad range of tests have been performed on wide range micro-alloyed SAC solders. Selected data is presented below to demonstrate the fundamental issues of bulk solder properties, IMC growth kinetics, solderability as measured by solder spread and alloy tarnish resistance.

SAC Alloy Composition

Figure 5 shows drop shock test data on SAC405, SAC305, SAC105 and SACX performed with CABGA100 components assembled with 18 mil spheres. The high Ag alloys consistently fail at lower cycles than the low Ag alloys. As discussed above, Figure 1, this is to be expected due to the lower modulus of the lower alloy solder and is an important factor in selecting solder alloys for high strain rate applications.

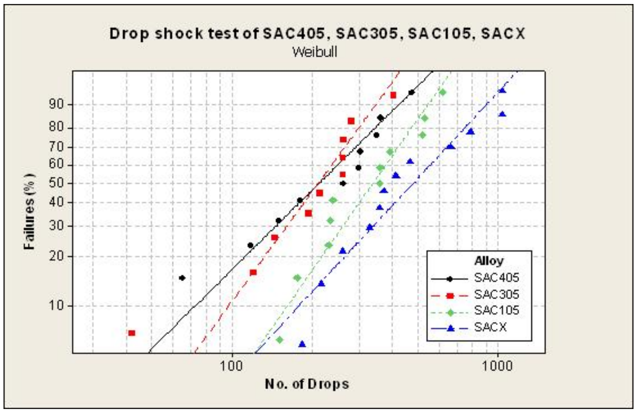


FIGURE 5: Drop shock tests for common SAC alloys.

Effect of Micro-alloying Additions

We have screened a large number of alloy additions in this work but here we limit ourselves to discussing the effect of Ni, Cr, Bi, Ge and In additions. The reason for this is that we wish to highlight the ability to engineer combinations of property improvements by considering the role the micro-additions play in the solder metallurgy and the IMC development during soldering and life testing.

Role of Bismuth

Cookson has developed a range of SAC alloys with improved wetting and spread. A component of these alloys is

Bi. Since a number of authors [11, 12] have discussed the effect of Bi on brittle fracture we wished to determine the performance of Bi modified SAC alloys in ball pull and drop shock.

Figure 6 and 7 show the ball pull data on SAC305, SAC205, SAC105, SAC0307 (SACX without Bi) and the same alloys with 0.1% Bi. These tests were done on CABGA100 chips with 18 mil spheres. After reflow the components were aged at 150°C for 500 Hrs before performing the ball pull test. The test speed was 15 mm/sec which is adequate to reveal brittle failure (mode 4) on aged solder assemblies.

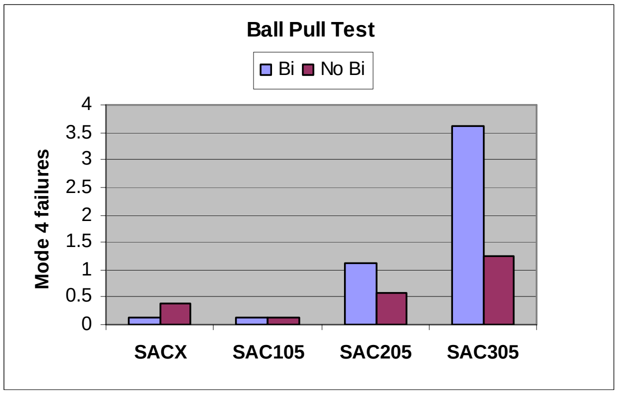


FIGURE 6: Ball pull tests for SAC alloys with and without 0.1% Bi additions

In Figure 7 a ratio of average mode 4 failures for each alloy with Bi addition without Bi addition has been plotted as a function of Ag level. A unity ratio means there is no effect of the Bi addition, a ratio >1 indicates an increase in mode 4 failures with Bi addition while a ratio <1 indicates an improvement.

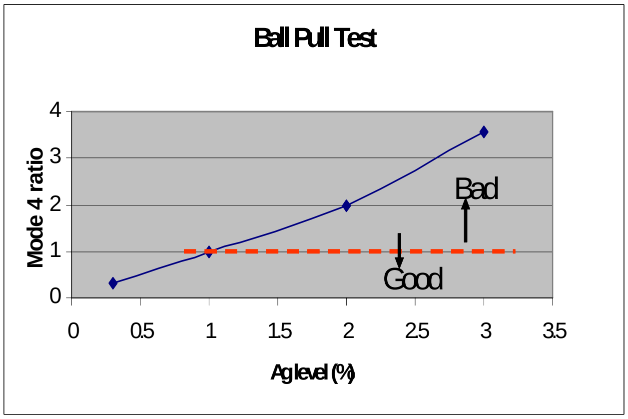


FIGURE 7: The ratio of mode 4 failures for SAC alloys with and without 0.1% Bi addition.

Weibull plots of the drop shock data for the same alloys, with and without Bi addition, are shown as in Figures 8 to 11. Like the ball pull data, drop shock data shows a negative effect of a Bi addition to SAC305 and SAC205, a marginal improvement in SAC105 and a large improvement in SAC0307 (SACX is SAC0307+0.1Bi).

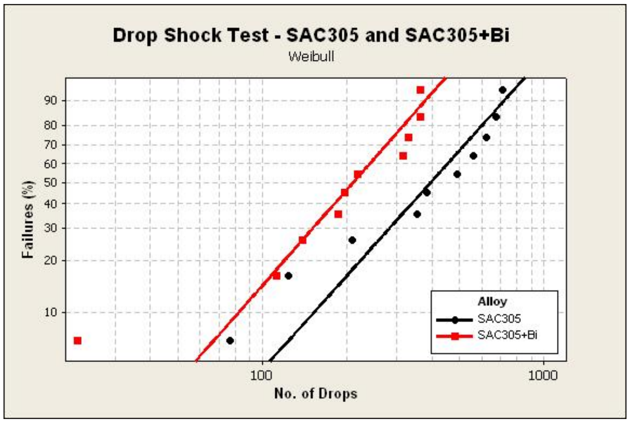


FIGURE 8: Weibull plot for SAC305 and SAC305 + 0.1% Bi

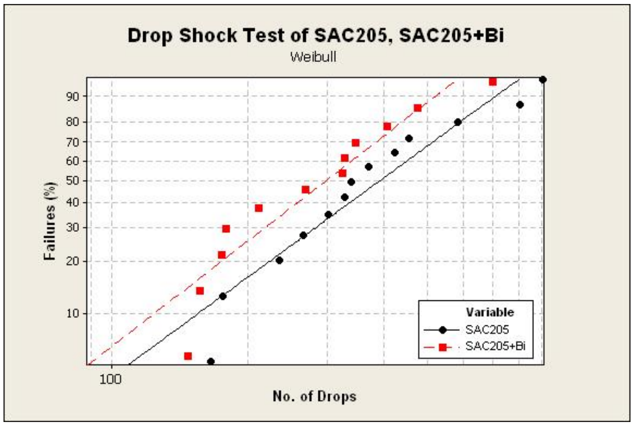


FIGURE 9: Weibull plot for SAC205 and SAC205 + 0.1% Bi

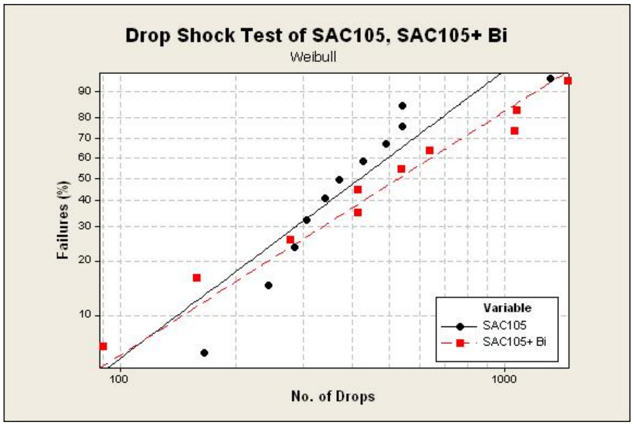


FIGURE 10: Weibull plot for SAC105 and SAC105 + 0.1% Bi

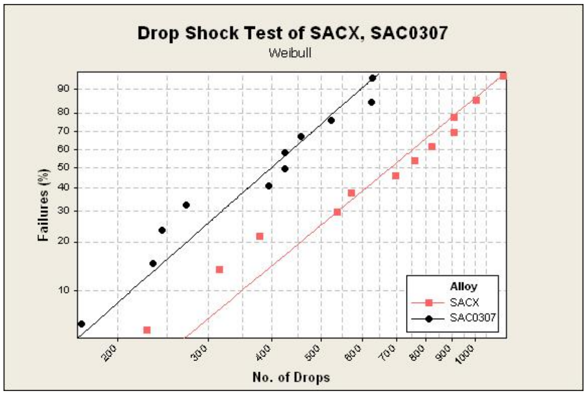


FIGURE 11: Weibull plot for SAC0307 and SACX

High Speed ball pull tests (at 1000 mm/sec) on CBGA84 components with 12 mil spheres on SACX alloy with different levels of Bi addition are shown in Figure 12. In addition to the mode 4 failures, solder spread on Cu-OSP is also plotted. The number of mode 4 failures decreases with increasing Bi level while solder spread increases.

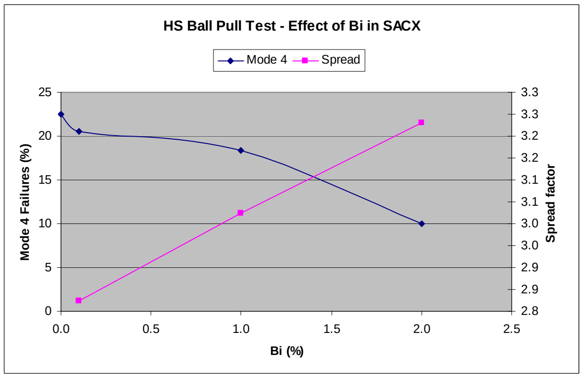


FIGURE 12: High strain rate ball pull test along side solder spread data for SACX at different Bi levels

In summary the effect of Bi additions on high strain rate failure in solder joints is highly alloy dependent. A clear reduction in mode 4 (brittle) failures are seen only for low Ag alloys (Ag < 1%). Large improvements are seen for SACX (Ag = 0.3%) that are extended to relatively high Bi additions, up to 2%. Figure 12 shows that the reduction in brittle failures with increasing Bi is accompanied with improvement in alloy wetting and spread.

Role of Ni, Cr

Ni and Cr are not common additives to SAC alloys however the potential effect of these additions on both the alloy microstructure and surface chemistry made them attractive for study.

The solder spread of SAC105 was measured with different levels of Ni addition, Figure 13. The reproducible optimum level for SAC105 is 0.05% Ni. The deterioration in spread at higher Ni levels is thought to be due to the formation of nickel oxides although interestingly good spread is achieved for increasing levels of Ni in SACX to over 0.1%.

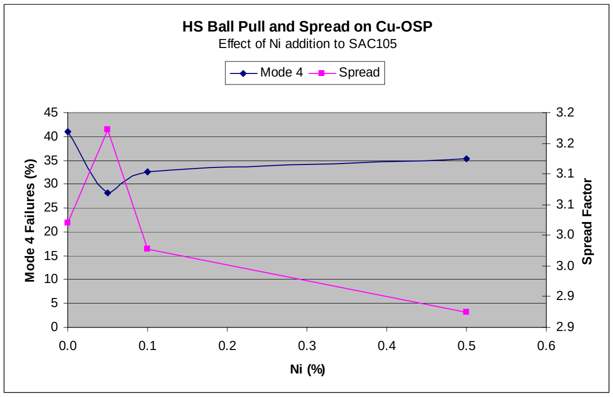


FIGURE 13: Solder spread of SAC105 on Cu-OSP as a function of Ni level together with ball pull performance.

Figure 13 also shows the ball pull results at the different Ni additions. There is a reproducible correlation between improved ball pull and solder spread. 0.05% Ni appears to be optimum level for both. The same is also confirmed by drop shock test shown in Figure 14.

Figure 14 reports drop shock results for SAC105 with 0.05% Ni and 0.5% Ni. The performance with 0.5% Ni is significantly poorer than 0.05% Ni. This is discussed below in terms of the increased IMC that forms on soldering to Cu with higher Ni alloys.

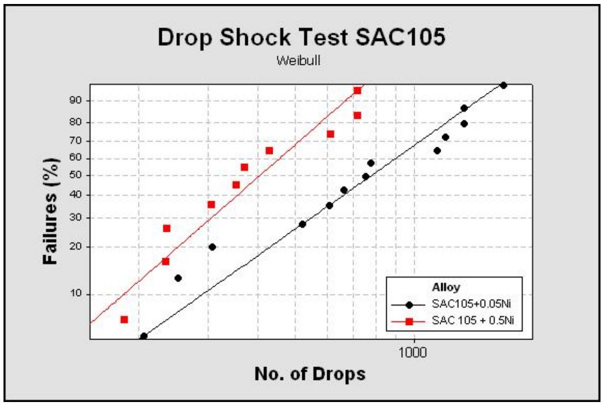


FIGURE 14: Drop shock data for SAC105 with 0.05% Ni and 0.5% Ni

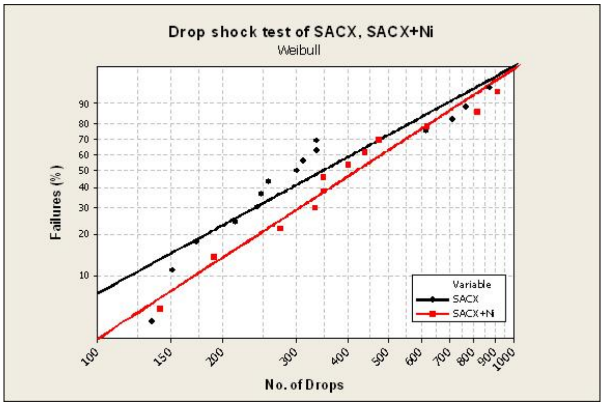


FIGURE 15: Drop shock comparison of SACX and SACX with 0.1% Ni addition. (CABGA100 chips assembled with 18 mil spheres)

Figure 15 shows the data for SACX with 0.1% Ni. In this case there is only marginal improvement in drop shock.

Cr has a zero to negative effect on solder spread. In conjunction with Ni however some reasonable improvement in spread can be demonstrated. Figure 16 shows an interaction plot of Ni and Cr levels in SAC105. A strong interaction is present and further optimization work is being carried out.

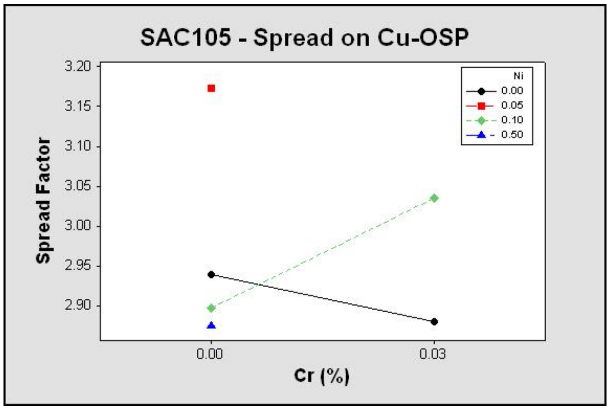


FIGURE 16: Solder spread of SAC105 on Cu-OSP with Ni plus Cr additions

It is in the area of mechanical properties that the addition of Ni and Cr is most effective. Figure 2, discussed above, shows the effect of 0.1% Ni in SAC305 soldered to Cu-OSP on Cu_3Sn IMC layer growth during aging at 150°C. This addition almost halves the critical brittle IMC growth through 500 hours aging. This reduction in IMC contributes to improved high strain rate testing performance as seen in the Weibull plots and ball pull data below.

Figure 17 compares drop shock for SAC105 with Ni, and SAC105 with Ni and Cr additions.

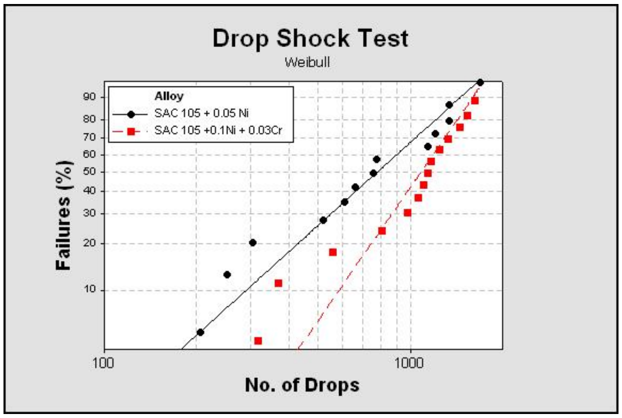


FIGURE 17: Drop shock data for SAC105 with 0.1% Ni and SAC105 with 0.1% Ni + 0.03% Cr

The high speed ball pull results on SAC105 with Ni, and Cr additions are shown in Figure 18.

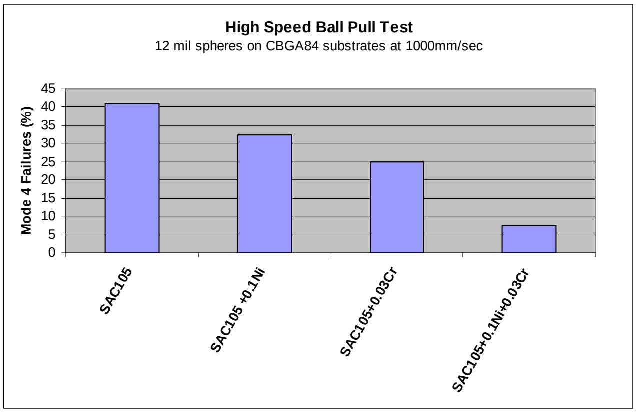


FIGURE 18: High speed ball pull results for SAC105, SAC105 with 0.1% Ni, SAC105 with .03% Cr and SAC105 with 0.1% Ni + 0.03% Cr.

SAC105 with 0.05% Ni shows ~30% less mode 4 failures in high-speed ball pull compared to SAC105 with no additions. Similarly 0.1% Ni and 0.5% Ni addition to SAC105 lead to ~20% and ~15% decrease in mode 4 failures respectively as compared to plain SAC105.

A 0.03% Cr addition to SAC105 reduces the fraction of mode 4 failures by ~40%. Importantly, and similarly to the solder spread results, there is a synergistic effect between Ni and Cr. While 0.03% Cr alone provides good improvement, the addition along with 0.1% Ni results in >80% decrease in mode 4 brittle failures. The collective effect of Ni and Cr additions is greater than the sum of the individual effects.

Role of Ge, In, Ni

Ge and In are, for different reasons, not common additions to Pb-free solders. Both are expensive elements and Ge has low solubility in Sn. In nevertheless has an attractive possibility as a diffusion compensator and Ge potentially can improve surface properties.

No clear wetting and spread advantage was seen for Ge or In. Some improvements in ball pull and drop shock were found. Figures 19 and 20 summarize this data for ball pull and drop shock respectively.

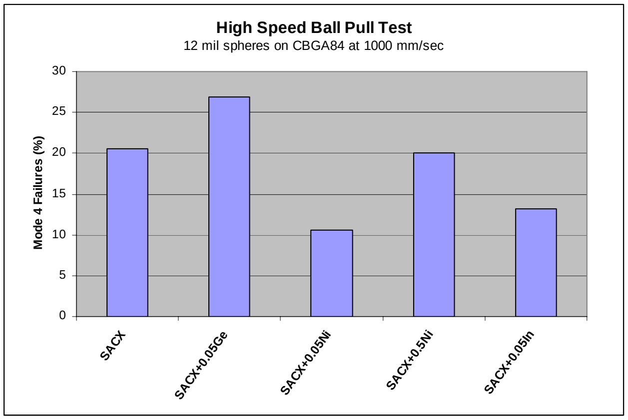


FIGURE 19: High-speed ball pull tests for SACX with different additives.

As shown in Figure 19, in high speed ball pull SACX with 0.05% Ni shows ~50% less mode 4 failures than unmodified SACX while a 0.05% Ge addition increases the same by >50%. 0.05% In offers ~30% reduction in mode 4 failures. While a 0.5% Ni addition shows as many failures as non-modified SACX.

Interestingly, unlike SACX, a 0.05% Ge addition to SAC105 results in ~20% drop in mode 4 failures in high speed ball pull.

Figure 20 shows the drop shock comparison of SACX with Ge, Ni and In additions and these follow closely the ball pull data.

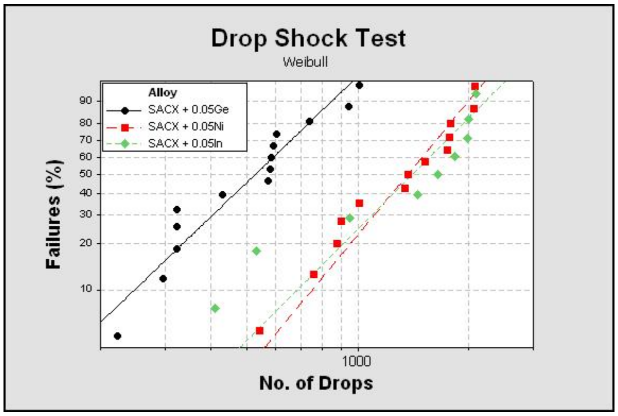


FIGURE 20: Drop shock comparison of SACX with Ni, Ge and In additions.

Tarnish Performance

Figure 21 shows the sphere color change as a result of thermal aging. Aging conditions were 12 Hrs at 125°C, followed by 168 Hrs at 85%RH and 85°C, then subjected to 3 times reflow at 255°C and 30 sec above 217°C. Basic SAC305 alloy spheres without any surface treatment turn brownish. A small quantity (~50ppm) of phosphorus addition eliminates that problem but the spheres still take on a yellowish hue. A Cr addition to SAC305 eliminates this problem altogether. A Ni addition also provides reasonable protection against tarnish.

FIGURE 21: Effect of alloy additives on the tarnish resistance of solder spheres. (12 Hrs aging at 125°C; 168Hrs at 85%RH and 85°C; 3x reflow in air at 255°C for 30 sec TAL)

Discussion

Effect of Bi addition

Bismuth additions to Pb-free solders have been the subject of many investigations. Bi can lower the solidus temperature, improve strength through precipitation hardening while suppressing the formation of large Ag_3Sn IMC in the bulk solder [11]. Segregation of Bi to the Cu/IMC interface is also reported [12]. IMC growth is reduced but there are implications for brittle fracture.

In this work the results show that the effect of Bi is highly beneficial. The addition, of up to 2% Bi, to SAC alloys results in improved wetting and alloy spread. The spread of the alloy is improved further by the addition of between 0.005 - 0.05% Ni. The improved spread can be interpreted in terms of surface segregation of the micro-alloying additions. Since Bi does not form an IMC with Cu, the presence of a high Bi concentration at the solder/Cu substrate interface is favorable to greater alloy spread. A similar argument can be made for other transition metals that do not readily form IMC phases with Cu at normal soldering temperatures.

The role of Bi in high strain rate failures is alloy dependent. A Bi addition to a high Ag alloys such as SAC305 reduces, for example, drop shock resistance – Figure 8. With reducing Ag content the negative effect is reduced until for SACX compositions (0.3Ag) the addition of Bi results in improved drop shock and bull pull response – Figures 8-11.

The addition of Bi reduces the IMC growth and, following Shang [13], the Bi may be expected to partition to the Cu/IMC interface. Since a higher modulus, high Ag alloy will transfer stress to the IMC interfaces a poorer response with a Bi addition is to be expected. Conversely, lower modulus, low Ag SAC alloys can harness the IMC control provided by Bi without risk of brittle failures. SAC105 (1%Ag) represents the transition point between a negative and positive effect of Bi on high strain rate testing.

Effect of Ni and Cr addition

The effect of low Ni additions to SAC alloys has been reported by several authors; see for example the excellent review by Tegehall [14]. While Ni is reported to make Cu_6Sn_5 more brittle as the ternary IMC it is also slows IMC growth on aging (150°C) – Figure 2

In our testing Ni has a strong effect on IMC growth and, at 0.05% addition, mode 4 ball pull failures are reduced by a third for SAC105 and nearly a half for SACX. Higher levels of Ni provide less improvement in ball pull results as might be expected from higher IMC growth rates during soldering [15].

Along with improved high strain rate behavior Ni offers two other benefits. At the optimum addition level (~0.05%) SAC alloys with Ni show greater solder spread – Figure 13, and Ni also provides a measurable improvement in solder tarnish resistance, an important consideration in BGA and CSP assembly.

Cr has no solubility in Sn so it is difficult to alloy into SAC solders. Our interest here was two fold, seeking a reduction in the modulus of the solder in conjunction with improvements in tarnish resistance. In low strain rate ball pull on SAC alloy with 0.03% Cr addition there is a reduction in the breaking stress compared to the alloy with no micro-addition. We interpret this in terms of the alloying effect of the Cr. Cr is alloyed via the Cu component in the solder and will limit the formation of Cu_6Sn_5 IMC in the bulk solder. Further, in high strain rate testing there is about a 40% reduction in mode 4 failures for SAC105 with 0.03% Cr – Figure 18.

The most important finding however is that Cr, synergistically with Ni, offers over 80% reduction in mode 4 failures. This is reproduced in the drop shock evaluation – Figure 17

Effect of Ge in SAC alloys

We have studied the effect of Ge in SAC alloys because of the potential again for improved corrosion behavior in conjunction with improvements in mechanical properties. The high strain rate results for 0.05% Ge addition alone are not positive. For SACX there is a one third increase in mode 4 failures.

Effect of In in SAC alloys

In, as an addition to SAC alloys is reported to reduce Kirkendall voiding but had little effect on the growth of Cu_3Sn IMC [16]. The role of In as a diffusion "compensator" is born out by Cookson's work on SnZn Pb-free alloy development, notwithstanding Amagai et al, in respect to SAC alloys In is reasonably effective in reducing mode 4 ball pull failures rating, for SACX, only behind Ni and Ni+Cr additions. Further work is underway to establish IMC growth kinetics for alloys with micro-additions of In.

Detailed failure analysis and documentation of the evolution of the alloy and interfacial microstructures is underway for selected alloys to support the phenomenological data presented in this paper

Conclusions

High strain rate testing of a family of Pb-free SAC alloys with micro-alloying additions has been carried out to identify viable candidates for BGA and CSP packaging applications. High rate ball pull results are consistent with industry standard drop shock testing results and clear improvement over un-modified SAC alloys is observed.

The data supports the following conclusions:

1. Low Ag SAC alloys are more resistant to high strain rate (drop shock) failure.
2. A number of micro-alloying additions are effective in improving drop shock performance. In particular a combination of Ni + Cr offers high drop shock reliability and excellent tarnish resistance
3. The addition of Bi together with Ni provides over 20% improvement in solder sphere spread on OSP Cu. This improvement is maintained for the Bi+Ni+Cr combination.
4. The best combination of properties is demonstrated for modified SAC105 and SACX with 0.05% Ni + 0.03% Cr.
5. For low Ag alloys (Ag <1%) Bi improves drop shock and ball pull performance. For high Ag SAC alloys Bi has a detrimental effect on high strain rate response.
6. Low Indium additions provide upto 30% reduction in mode 4 failures in high-speed ball pull for all SAC alloys. The addition of In to SAC alloys does not improve SAC alloy wetting and spread.

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