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PROCESSING AND RELIABILITY OF LOW-SILVER-ALLOYS

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ABSTRACT

The change from lead to lead-free solders is underway since several years. After consumer and IT industry, the European automotive industry has also to make efforts to adapt lead-free solders till 2011. First major product runs for lead-free automotive electronics will be expected already for the next year. Besides some other alternative alloys, Sn-Ag-Cu solders became worldwide accepted and are already widely used. But the drawback of lead-free technology is the growing expense of materials and processes. Therefore the attempt has been made to reduce the costs on the material side within the realms of possibility. The decrease of silver content of solders can have a share in cost reduction. At present especially in Asia some projects are being executed with low-silver alloys for mobile communication and furthermore for automotive electronics. The wetting behaviors of low-silver alloy SnAg1.0Cu0.5 are comparable to a considerable degree with eutectic standard SnAg3.0Cu0.5 and can be used mostly as a "drop in" solution. Certainly a matt surface should be considered for optical inspection. In contrast to SnAg0.3Cu0.7 a wider melting range already influences the wetting behaviors considerably. Therefore the soldering parameters must be especially adapted for this very low-silver alloy. But with matching soldering temperature a good solderability is also possible. Besides the processing conditions, the reliability of test boards for solders with a different silver content after thermo-cycling will also be compared.

Key words: lead-free, solder joints, reliability, processing

INTRODUCTION

Looking at the price development of materials on the market, a permanent up and down is visible. This is the case for base metals like copper and tin [LME-08] and even more dramatic for precious metals like silver [FTD-08], shown in figure 1.

Figure 1. Price trend for silver on the global market in US Dollar [FTD-08]

These extreme up- and downturns also influence significantly the prices of solders alloys like tin-silver-copper with usually 3...4 wt% silver. Accordingly the reduction of silver content could minimize the price fluctuations in principle. The technical feasibility and the limits of this silver variation was the matter of investigation, presented in this contribution.

MATERIAL SELECTION

For the selection of capable solder alloys the variation range in respect of silver content should be defined. The eutectic point of the ternary alloy according to the phase diagram is located at roughly 3.8 wt% Ag and 0.8 wt% with a melting point of 217°C (423°F). Certainly it must be considered, that the chemical composition of solder is changing during the soldering process. Usually copper is used as a base metal in the solder joint, so this copper will be solved additionally into the solder joint. The composition of material in the solder joints is different from the original solder alloy; that is why this material could be called strictly speaking as solder metal. Because of the high solubility of copper in lead-free solders it is assumed that some microns of copper pad will be solved in the solder during a common reflow process. Based on an average solder paste thickness of 150µm (50 vol% solder), this corresponds with an increase of 1.5 wt% copper content per solved micron copper. Thereby the copper content exceeds in any case the eutectic point of tin-silver-copper alloy. That is the reason for minimizing the copper content of such solders in the initial composition, usually with 0.5 wt%.

Furthermore for optimizing of solder alloys it has to be taken into the account that both elements, Ag and Cu form intermetallic phases with Sn. Especially the Ag_3Sn intermetallic phase causes plate shaped structures in the solder joint, which are critical for the reliability. Therefore the silver content in solder alloys is usually also reduced from the eutectic point, common are solders with 3.0 wt% Ag and 0.5 wt% Cu. Additionally the tolerances of composition have to be incorporated, for alloy components with those concentrations are ±0.2 wt% usual. This makes clear other disadvantages of lead-free solders compared to the traditional tin-lead. On the one hand it is possible to produce Sn63Pb37 more simply with rougher tolerances, e.g. ±0.5 wt%. On the other hand the tin-lead alloy does not form intermetallic phases. Furthermore, the lead content inhibits the dissolution of copper at the interface and so the growing of intermetallic phases.

For the selection of reduced silver content for the investigations it must be considered, that silver and copper decrease the melting point of the solder, which also allows the lowering of soldering temperature. The melting point of pure tin is 232°C (450°F) whereas the eutectic SnAg3.5 melts already at 221°C (430°F). Regarding the part of the phase diagram, shown in figure 2, it is visible how the decrease of silver content influences the melting range. While the solidus temperature is constant at 221°C in this range, the liquidus temperature could increase up to the melting temperature of pure tin. Much more critical would be an increase of silver content, because the rising of liquidus temperature is steeper in this direction. Although for a soldering temperature below liquidus the flowing and wetting of solder are possible, the solder would be incomplete molten with an amount of solid particles. This influences the structure of the solder joint. It is possible to calculate the amount of solid particles in the melt depending on temperature and silver content by the lever-rule from phase diagram. To enable the flowing and spreading of solder an amount of liquid phase much more than 50 vol% is needed.

Displaying of the ternary phase diagram Sn-Ag-Cu is more difficult, but the relations are comparable with the binary Sn-Ag system in principle. Because the binary Sn-Cu melts at 227°C (441°F), the liquidus temperature in the ternary system can increase by minimizing of silver content only up to this temperature. The eutectic temperature of the ternary system is 217°C, so the solidus temperature should also be in this range for lower silver content in the solder.

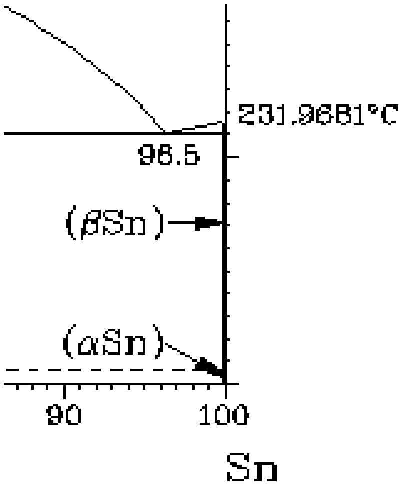

Figure 2. Phase diagram of the binary Ag-Sn system in detail (tin rich side) [ASM-96]

Regarding these considerations the choice of silver content for the investigations is possible between zero and 3 wt%, certainly with respect to the manufacturing tolerances. In what follows two silver reduced alloys with 1 wt% and 0.3 wt% were used for experimental works.

COMPARISON OF PHYSICAL PROPERTIES

An important difference between eutectic and low-silver Sn-Ag-Cu consists in the dissimilar liquidus temperatures, as mentioned before. Non-eutectic solders have a melting range instead of a melting point. This range was investigated by temperature measurements for selected alloys. Therefore the solders, each with 50 grams in a ceramic crucible, were heated in a controlled oven with a thermal analyzing system. Besides the silver-reduced alloys SnAg1.0Cu0.5 and SnAg0.3Cu0.7 also the standard solders SnAg3.0Cu0.5 and SnAg3.5 were investigated as a reference. Both the heating and the cooling rate were defined with 1 K/min. Figure 3 shows only the heating part of this curves with the melting behaviors of all four alloys.

The analysis of thermal behaviors shows some quantitative and qualitative differences of alloys. The eutectic SnAg3.5 offers a clear temperature hold point during melting and solidification at 221°C as expected. Moreover the near-eutectic SnAg3.0Cu0.5 has only a small melting range between 217°C and 220°C. Already for the SnAg1.0Cu0.5 solder a wider melting range between 217°C and 227°C is visible. This range expands even to 217.5°C and 229°C for SnAg0.3Cu0.7. This means that silver-reduced solders start to melt already at 217°C, but the complete melting needs 10 K higher soldering temperatures. The spreading and wetting behaviors could be influenced by these properties, even if the soldering temperature of 230°C is achieved or exceeded.

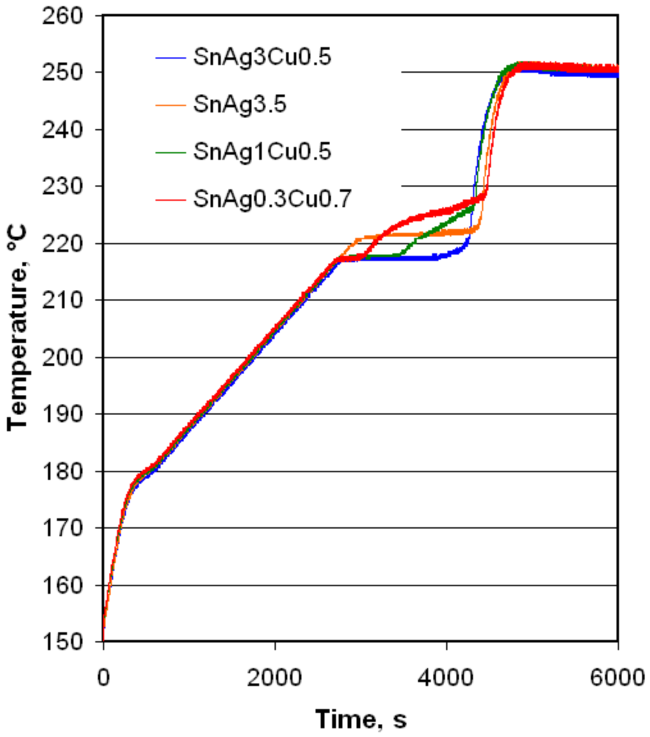

Figure 3. Measured heating curves of selected solder alloys with different compositions

alloy	Solidus temperature, °C	Liquidus temperature, °C
SnAg3.5	221	221
SnAg3.0Cu0.5	217	220
SnAg1.0Cu0.5	217	227
SnAg0.3Cu0.7	217.5	229

Table 1. Melting behaviors of selected solders

SOLDERABILITY

In the simplest case it is possible to test the solderability of alloys on real printed circuit boards, here OSP-surface finishes, by a solder spreading test. This could be made under process conditions. Therefore four solder paste depots at a time were printed with a 150 µm stencil and an aperture diameter of 8.2mm on the test PCBs. All four solder pastes contained the same flux system and were soldered with the same process conditions at 230°C. Besides a more matt appearance the wetting result of the silver-reduced and standard alloys is nearly the same. The quantitative measuring of wetting areas under microscope offers diameters between 8.1 and 8.3 mm or an area between 51 and 55 mm^2 for all four solders, which corresponds with the printed surface on PCB. The negligible differences of wetting areas are also visible in the diagram in figure 4.

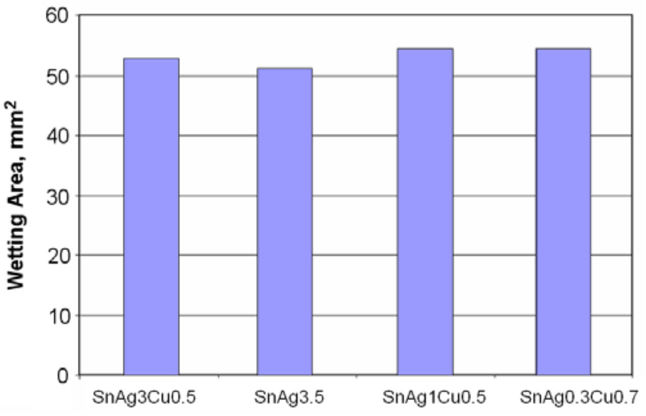

Figure 4. Average wetting areas of different solders on an OSP surface finish

Additional information about wetting dynamics could be gathered by measuring with a wetting balance analyzer, where the test conditions should correspond with the process conditions as much as possible. The solder globule method with 130 mg solder at 235°C (455°F) test temperature was applied for the present investigation. Lead-free tin coated pins of a usual Pentawatt-5 IC were used as a test sample. These pins were dipped in the molten solder globule with 1 mm depth for 10 seconds by means of a flux identical with the solder paste system. The registered force-time-graph could be interpreted for evaluation of dynamic wetting behaviors.

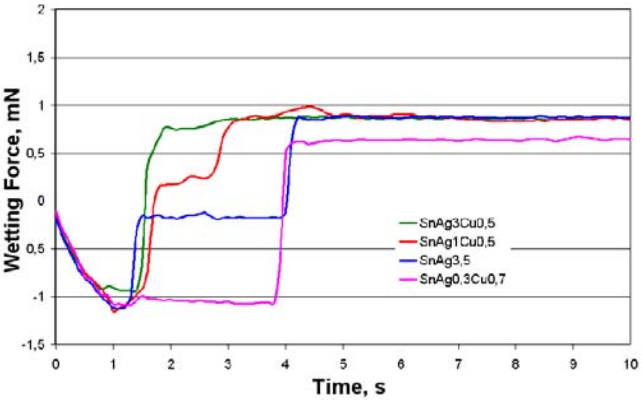

Figure 5. Wetting graphs for different solder alloys, measured with the solder globule method at 235°C

Qualitative differences are visible already in the shape of the graphs. However the SnAg1.0Cu0.5 solder shows the most similar appearance like standard solder SnAg3.0Cu0.5. The evaluation of wetting forces and wetting times results from averaging of some graphs. Resulting from this evaluation in figure 6, only the SnAg0.3Cu0.7 alloy shows significantly lower wetting forces.

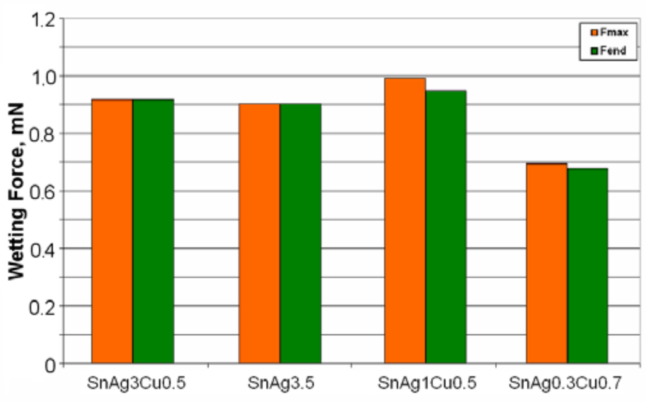

Figure 6. Evaluation of average wetting forces, tested with the solder globule method at 235°C

Clearer differences could be observed for the wetting time, which shows for SnAg0.3Cu0.7 as well as for SnAg3.5 more than double time for wetting (see figure 7).

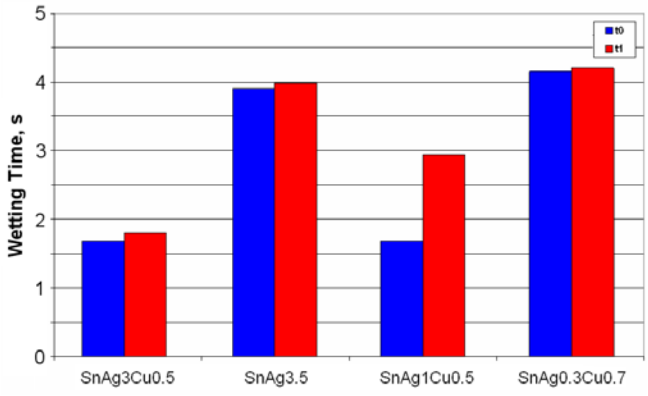

Figure 7. Evaluation of average wetting times, tested with the solder globule method at 235°C

In addition to measuring of wetting by the solder globule method, the solder paste method was used. For it a defined amount of solder paste was printed on a copper substrate and then heated on a heat plate up to soldering temperature of 240°C (464°F). The temperature ramp was set to 3 K/s. A copper cylinder with 5 mm diameter und 0.5 mm wall thickness was used as a test sample. This was immersed at depth of 150 µm in the printed solder paste. Variation of wetting force during wetting with the molten solder was also registered.

Because of the interaction of solder powder and flux in the solder paste, the interpretation of wetting graphs is more difficult and a standard curve with comparable values is hardly recognizable. In this case the gradual melting of the melting-range solders leads to more than one maximum and minimum in the graph. The graph of the low-silver SnAg1.0Cu0.5 is at least similar to the eutectic SnAg3.5. Finally all graphs lead into nearly the same maximum wetting force, shown in figure 8. An evaluation of wetting times is more difficult because of the multiple maxima, so that the results in figure 9 are not very reliable.

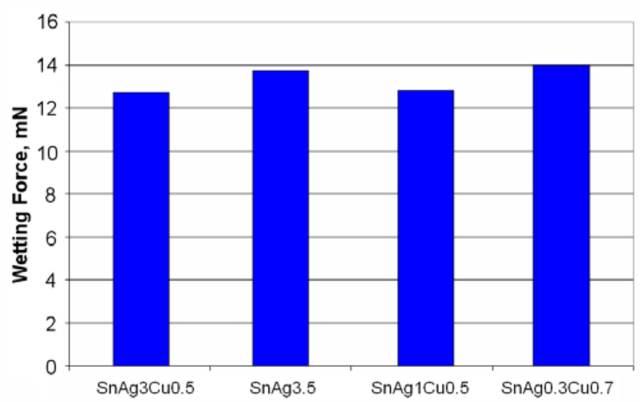

Figure 8. Evaluation of average wetting forces, tested with the solder paste method at 240°C

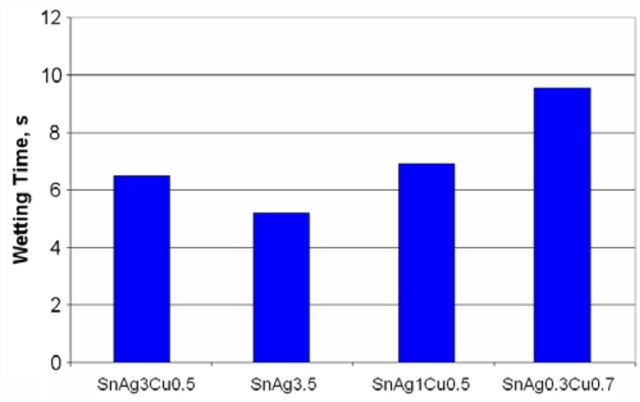

Figure 9. Evaluation of average wetting times, tested with the solder paste method at 240°C

Aside from these standard evaluations also the slope of wetting force was calculated, which is more than ten times faster for SnAg3.0Cu0.5 than for the other alloys.

PROCESSING AND BENCHMARKING

On an internal used benchmarking testboard the usual processing tests for printing, solder balling, slumping and wetting were made. As expected, the printing and application of solder pastes show no significant differences for all four solder pastes. On the immersion tin surface finish it could be noticed, that the (near) eutectic standard solders SnAg3.0Cu0.5 and SnAg3.5 show a little better wetting than low-silver alloys SnAg1.0Cu0.5 and SnAg0.3Cu0.7. This could be explained not only by the wetting or solder spreading on the tin surface, but also by the different surface properties of the solder itself. Figure 10 shows examples of soldered chip capacitors with the size 1206 on the benchmarking testboard. The brightness of the solder joints is obviously different: it is more matt for the non eutectic solders. Not visually recognizable at once is the different shape of the joints. The measurement of the surface line with an automatic laser sampling gives more information about the wetting angle at the component. These angles are also specified in the same figure 10. For the standard SnAg3.0Cu0.5 this angle is considerably lower and increases for the low-silver alloys with decreasing silver content. This could be also an indication for a different surface tension or viscosity.

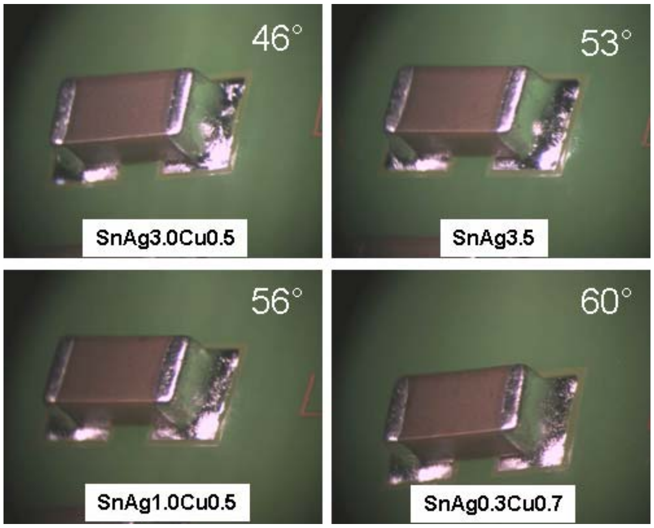

Figure 10. Optical inspection and measured angle of solder joints at chip capacitors 1206

It could be assumed that the higher wetting angle and the detected melting range of low-silver solders is possibly also an advantage for preventing from tombstone effect. Therefore a statistical tombstone test on a special testboard [TROD-07] was done. But the evaluation of this test shows, that the influences of layout and components predominate the tombstone effect. The properties of low-silver alloys are nearly the same as the near eutectic SnAg3.0Cu0.5. Only the exact eutectic SnAg3.5 causes a slight increase of tombstones.

RELIABILITY

Besides the processing behaviors of low-silver alloys the properties of use are at least just as important. That includes the mechanical stability, i.e. strength or creeping, the chemical resistance against diffusion and corrosion and the changing of these properties depending on time of use, which means the reliability. Therefore accelerated aging of soldered testboards were leaded through. A thermal storage with 125°C for 1000 hours and a temperature cycling between -40°C and +150°C for 1000 cycles (so far) belongs to these aging tests. After different steps of aging a destructive testing of solder joint strength follows, realized with a shear test, combined with the metallographic analysis of selected solder joints with cross sections.

Present results of thermal aging for 1000 hours show now the significant changing of strength and negligible difference of solder alloys in shear strength. The results after temperature cycling are different. The drop of strength after this aging amounts to 16% to 34% for the different alloys. Unexpected was the dimension and order of these values. While SnAg1.0Cu0.5 shows the highest loss of strength after cycles, SnAg0.3Cu0.7 offers the highest stability and smallest loss, shown in figure 11. So the silver content could not be the only cause for this effect. The metallographic analysis should give more clearing up.

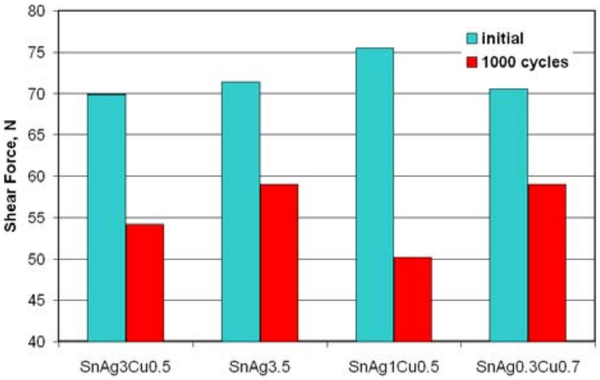

Figure 11. Drop of shear force for solder joints after 1000 temperature cycles between -40°C and +150°C

Figures 12 and 13 show examples for the solder joint structures after 1000 cycles for SnAg1.0Cu0.5 and SnAg0.3Cu0.7. Besides the different outer shape and grain coarsening the thickness and structure of solder gap in the joint is also different.

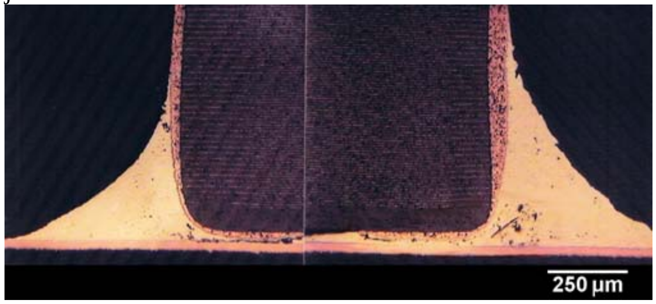

Figure 12. Cross section of a SnAg1.0Cu0.5 solder joint of a CC1206 component after 1000 cycles

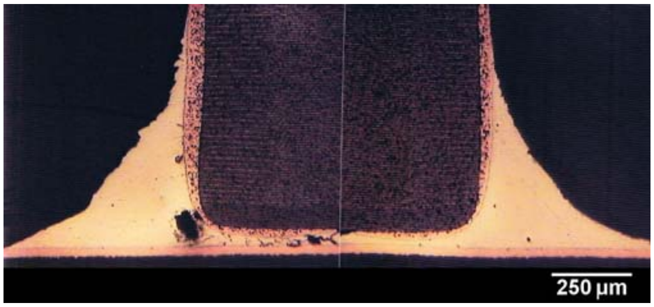

Figure 13. Cross section of a SnAg0.3Cu0.7 solder joint of a CC1206 component after 1000 cycles

A measuring of intermetallic compound thicknesses at the interfaces to component and printed circuit boards shows also different values for all four alloys. The standard alloys SnAg3.0Cu0.5 and SnAg3.5 have a slightly thinner intermetallic layer with an increase after aging. Whereas the silver-reduced solder joints have a thicker intermetallic layer already in the initial state, but a smaller increase after aging for SnAg0.3Cu0.7. Besides the different silver content it could be supposed, that the minor difference of copper content will also influence the reliability.

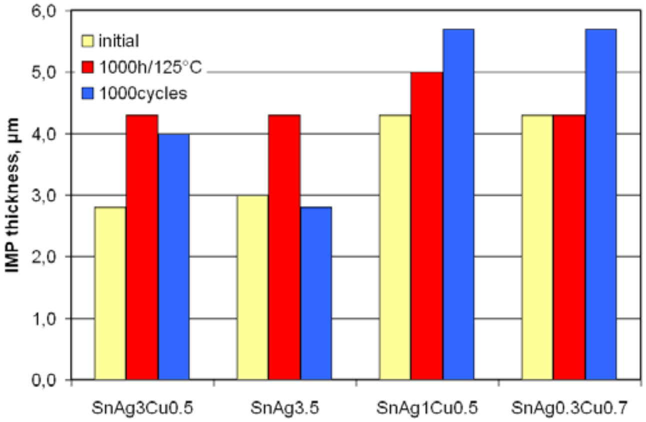

Figure 14. Measured thicknesses of intermetallic phases on the component side of the solder joints

CONCLUSION AND OUTLOOK

The soldering and wetting properties of the silver reduced alloy SnAg1.0Cu0.5 correspond to a considerable degree to the standard solder SnAg3.0Cu0.5. But the more matt surface of the solder joints has to be considered for the optical inspection. However the increased melting range of the SnAg0.3Cu0.7 alloy already influences the wetting behaviors. Therefore the soldering temperatures should be adapted especially for the use of this very low-silver solder. A satisfactory processing is also expected for a sufficient high soldering temperature. Surprising was the improved reliability especially for this very low-silver alloy, which shows the best results of all four alloys. The influence of copper and the further development for a higher number of temperature cycles should be the subject for a future investigation.

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