Composite soldering materials for high-temperature stable solder joints

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Abstract

The thermal load on electronic assemblies is constantly increasing. The reasons for this increase are, on the one hand, the integration of power electronic components in an ever smaller space and thus an increasing power density and, on the other hand, the increasingly harsh environmental conditions with high temperature load. In addition to electronic components and substrate materials, the soldered connections are also exposed to this stress and must withstand it. The thermal stability is primarily determined by the melting temperature of the solder material or by the remelting temperature of the final solder interconnection. The remelting temperature can be purposefully increased through diffusion soldering. The advantage of diffusion soldering is that the operating temperature of the final solder joint can exceed the joining process temperatures. By using the composite soldering materials and diffusion soldering process it is possible to produce the solder interconnections that can withstand the high thermal and thermo-mechanical stress [1].

In this work, the composite solder material, consisting of the base solder alloy BiSnAg in eutectic composition with a melting point of 139 °C and added copper particles, was examined. The added copper particles have a direct influence on the dynamics of the diffusion process. Diffusion can also be influenced by adjusting the soldering process parameters, such as maximum temperature and time above liquidus of the base solder alloy, with the aim of achieving isothermal solidification. The solidification can take place through the parallel reactions: the reaction between tin and copper with the formation of high-melting intermetallic phases Cu3Sn and Cu6Sn5 and the growth of bismuth crystals through coarsening of the structure and tin depletion in the original eutectic solder alloy [2].

Key words

Diffusion soldering, low-temperature solders, intermetallic phases

I. Introduction

The process of soldering is mainly used in the assembly and interconnection technology for the electronic modules. The thermal stability of the final solder interconnections is limited by the melting temperature of the solder alloys. Numerous investigations have shown that the value of the homologous temperature for the solder alloys should not exceed the value of approx. 0.8 for safe operation [3]. For the most commonly used lead-free near-eutectic alloys like SnAgCu and SnAg, this means a maximum allowable operating temperature of approx. 125 °C for the solder interconnections.

A potential alternative to these lead-free alloys is the low-melting solder alloy BiSn42 or BiSn42Ag1. The lower melting point of 138 °C or 139 °C respectively allows soldering processes to be carried out at a lower peak temperature and, as a result, there is a significant reduction in the thermal energy required for this, which can reach up to 40 % [4]. In addition to the reduced energy consumption, lowering the processing temperature enables the use of materials and components that are less thermally stable, such as substrate materials with lower T_g values or optoelectronic components.

At the same time, however, the low melting temperature leads to a reduction in the maximum allowable operating temperature. The maximum allowable operating temperature for the eutectic BiSn or BiSnAg alloy is approx. 80 °C. In order to increase the temperature resistance of the final solder connections, the diffusion soldering process can be used to achieve a transformation of solder joints into higher-melting intermetallic phases.

Such processes as SLID (Solid Liquid Inter-Diffusion) and TLPS (Transient Liquid Phase Soldering) are based on this mechanism. A similar approach was implemented in the project for the development of new interconnection technologies for use in high-performance modules in electro mobility (HPC), where a new technology based on mixing the lead-free standard alloy SnAgCu or SnCu in the form of solder paste with copper powder or copper paste was developed [5].

In the present work, an alternative approach to diffusion soldering is pursued, in which the precipitation and growth of crystals of pure bismuth are thermally accelerated in the low-melting alloy BiSn42 or BiSnAg1, the soldered joint solidifies isothermally and the remelting temperature is increased. The addition of copper particles is intended to further accelerate this process and increase the growth of high-melting intermetallic phases.

II. Sample preparation

The benchmark circuit board from the Institute for Electronic Appliances and Circuits was used to produce the samples. The chip resistors of various sizes from CR0402 to CR2512 are assembled on this circuit board, which are used to investigate the aging of the solder joints by measuring the shear strength after T-cycles. In addition, structures are positioned to qualify the solder paste print and the solder spread. The metallization of the printed circuit board is ENIG and the connections of chip resistors are tinned and have a diffusion barrier layer of nickel with a thickness of approx. 5 µm.

The solder paste of eutectic alloy BiSn42Ag1 (BSA) was applied using a semi-automatic stencil printer and a stencil with a thickness of 120 µm. The soldering process was realized in a convection oven with four heating zones and in a vapor phase soldering system with the medium Galden LS230. Based on the specifications of the solder paste manufacturer [6], the reference soldering profile was evaluated. The following requirements were considered: the time from room temperature to the temperature peak is 150-240 s, the time above liquidus is 45-75 s and the peak temperature is 155-180 °C. For the other temperature profiles, the peak temperature was successively increased and the conveyor speed reduced in order to achieve a higher heat input during the soldering process. Table 1 summarizes the soldering process parameters and Fig. 1 shows the resulting soldering profiles. To compare the heat input, the so-called heating factor was also calculated, which depicts the area between the soldering temperature and the liquidus line [7]. In this area, the interaction between the base alloy in liquid form and solid parts of the compound takes mainly place.

Table 1. Soldering process parameters of convection oven / vapor phase soldering machine

Nr.	name	zone 1	zone 2	zone 3	zone 4	conveyor, m/min	Heating factor, K*s
1	BSA-01	100	120	140	220	0,45	2.058
2	BSA-02	120	150	180	220	0,25	9.267
3	BSA-03	120	150	200	240	0,2	17.322
4	BSA-04	120	150	220	260	0,2	21.943
5	VP230	-	-	-	-	-	13.010

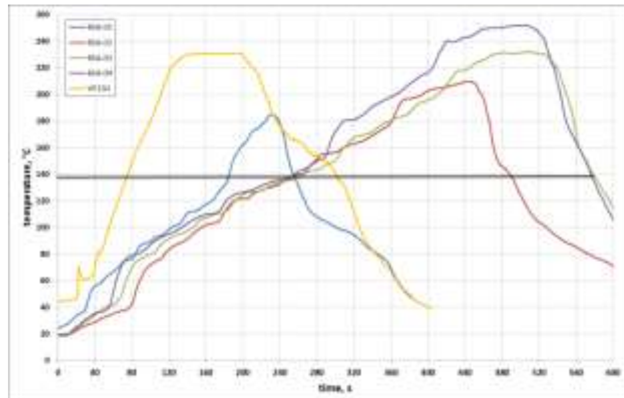

Fig. 1 T-profiles used to remelt the BSA solder paste

The solder paste DP5600 from the alloy Bi57Sn42Ag1 (BSA solder) from Interflux was used as the solder material. The solder paste has the powder type 3 (25-45 µm) and the solder powder content is 90 % by weight. Copper particles in flake form with a size of less than 45 µm were mixed into this paste to produce composite soldering materials. The size and shape of the particles has a great variation (Fig. 2). The irregular shape results in a higher surface area of copper in contact with the BSA solder that is available for interdiffusion. The proportion of copper particles is 5 % by weight of the total solder paste weight. Assuming the volume fraction of the solder alloy in the solder paste to be 50 % and knowing the densities of the BSA solder of 8.64 g/cm³ and copper of 8.92 g/cm³, the volume fraction of added copper in the final solder joint should to be about 10 %.

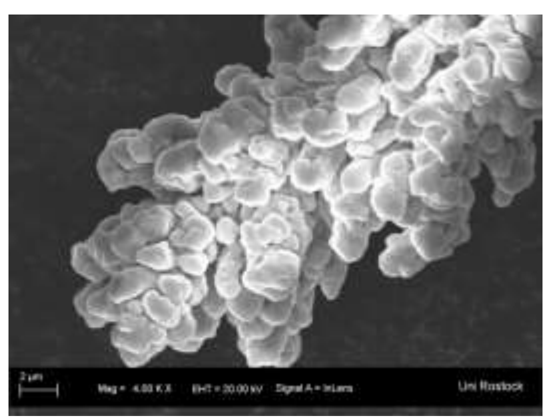

Fig. 2 Agglomeration of copper particles (4000x)

For additional heat input, the samples were exposed to a short-term thermal aging at 150 °C for 10, 20 and 30 minutes after the soldering process, and to a long-term thermal aging at 150 °C and 175 °C for 168 h.

III. Investigation of the solder joint microstructure

A. Influence of the soldering process parameters

After the soldering process, cross-sections were made of the CR2512 and CR0603 components and examined using a light microscope. The height of the solder gap varies between 10 and 30 µm. A particularly higher solder gap of up to 75 µm was observed in the samples with the added copper particles (Fig. 3).

Fig. 3 Solder joint BiSnAg+Cu produced with BSA-01 profile (1000x)

The microstructure was examined using light microscopy and scanning electron microscopy. Fig. 4 shows the SEM images of the soldered connection of the CR2512 component in the meniscus area after standard profile without/with copper particles. No significant coarsening of the structure or phase segregation could be observed, only increased growth of the intermetallic phase at the interface to the printed circuit board metallization.

With the help of the SEM/EDX analysis, the structure in the meniscus area and in the solder gap of the CR2512 component was analyzed for its composition. No significant differences could be determined. However, in the sample that was produced with the BSA-01 soldering profile and has the smallest solder gap of 10 µm, some areas with a particularly high concentration of bismuth were detected in the solder joint (Fig. 5).

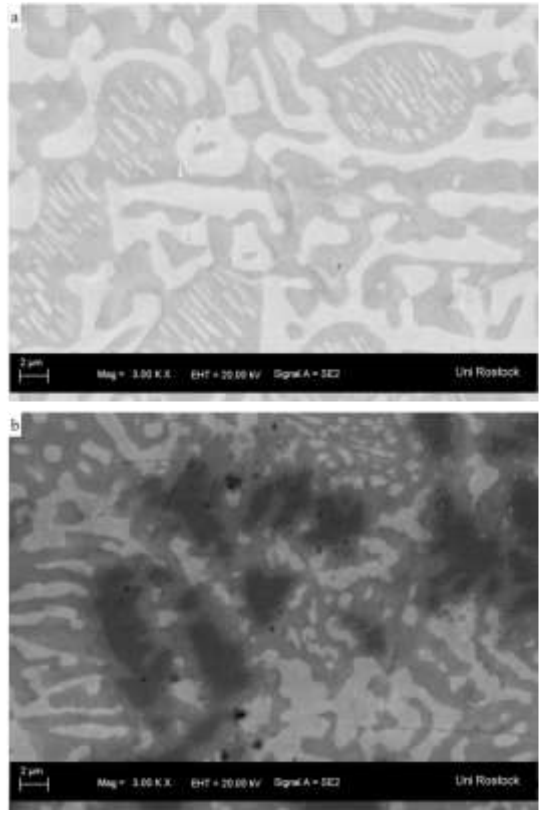

Fig. 4 Solder joint CR2512 produced with BSA-01 profile without (a) /with (b) copper particles (3000x)

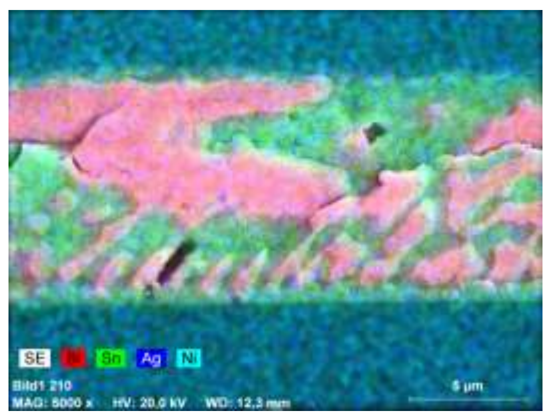

Fig. 5 EDX analysis of microstructure in the solder gap; solder joint BiSnAg produced with BSA-01 profile (5000x)

In addition to the Bi-rich areas, Sn-rich areas were also detected close to Bi, which indicates phase segregation. Solidification in this form is obviously favored by the small solder volume. However, the Bi precipitation does not bridge the entire solder gap. There are other areas with eutectic structure that determine the remelting temperature. The needle-shaped intermetallic phases Ag_3Sn formed during solidification can also reach a length of more than 10 µm. Fig. 6 shows the Ag_3Sn phases with 15 µm length.

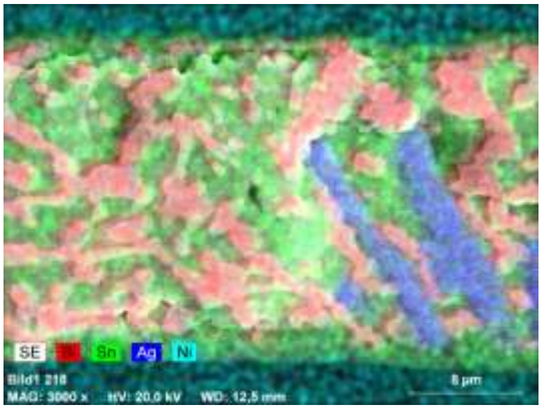

Fig. 6 EDX analysis of microstructure in the solder gap; solder joint BiSnAg produced with BSA-04 profile (3000x)

Of particular interest is the sample with added copper particles of 10 % by volume in the BiSnAg alloy. The copper particles were sufficient wetted during the soldering process and distributed in the solder joint. Copper reacts with the surrounding tin during the process, resulting in the formation of intermetallic Cu_6Sn_5 phases. The surrounding base alloy is depleted of tin, which accelerates the formation of Bi-rich areas (Fig. 7).

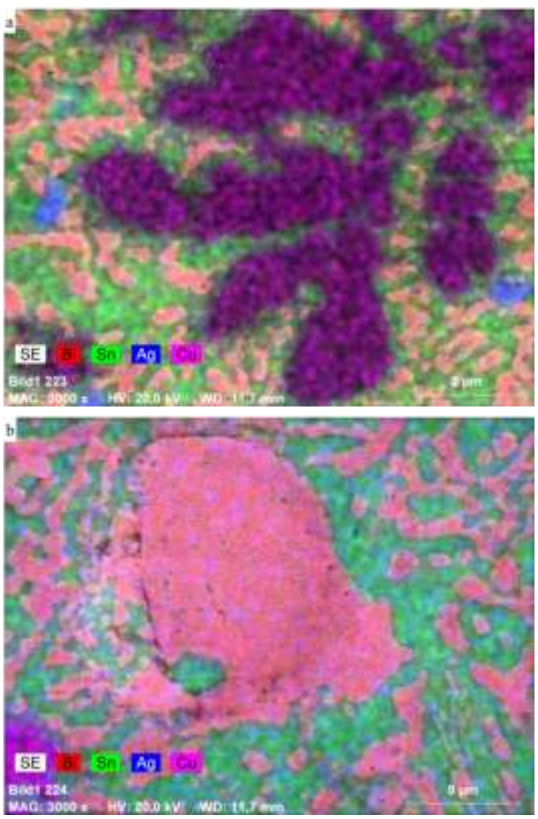

Fig. 7 EDX analysis of microstructure in the solder gap; Solder joint BiSnAg+Cu produced with BSA-04 profile (3000x)

With the BiSnAg alloy used, a local phase coarsening and precipitation of larger Bi crystals was observed in some samples with a specific combination of influencing factors such as soldering profile and heat input, composition of the alloy and the geometric conditions or volume of the solder interconnection. However, in the variants examined, complete bridging of the solder gap by such Bi precipitations (not even in combination with the other intermetallic phases in the solder interconnection) could not be observed and reliably produced. In the next step the modification of the microstructure of the solder interconnections through subsequent thermal aging was tried.

B. Influence of thermal aging on the microstructure of solder joints

After the soldering process, some samples were also aged at 150 °C for between 10 and 30 minutes. Then the cross-sections of the components CR2512 and CR0603 were made and examined with a light microscope. Fig. 8 shows the microstructure after the standard soldering profile and additional thermal aging.

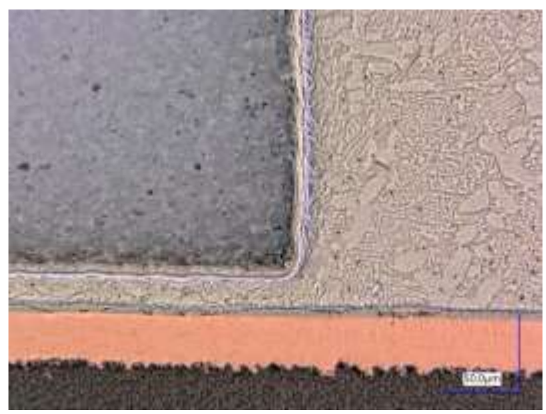

Fig. 8 Solder joint produced with BSA-01 profile / after thermal aging 30min at 150°C (1000x)

Regardless of the aging time, no significant coarsening of the structure was found in the samples. The heating factor for the thermal aging and the heat input above the liquidus is comparable to a prolonged soldering process (BSA-04). The increased precipitation of Ag_3Sn phases and their enlargement or transformation from needle shape to platelet shape could be observed. A similar effect for the formation of Ag_3Sn phases in a SnAg3.5 alloy was described in [8].

In order to achieve the desired effect, the heat input has to be increased, which can be done on the one hand by increasing the temperature and on the other hand by extending the aging time. Further samples were produced in two variants with and without additional copper particles with the standard soldering profile BSA-01 and then aged at two temperatures of 150 °C and 175 °C for 168 hours each. Numerous changes in the microstructure were detected during light microscopy and additional SEM/EDX analysis of metallographic sections. In the samples without copper particles, a thicker intermetallic Ni_3Sn_4 was observed at the interfaces to the circuit board and component metallization. With a small solder gap of approx. 10 µm, this partially led to complete bridging (Fig. 9). Since the melting temperature of the Ni_3Sn_4 phase is 796 °C, the bridging in the solder gap leads to a corresponding increase in the remelting temperature of the solder joint.

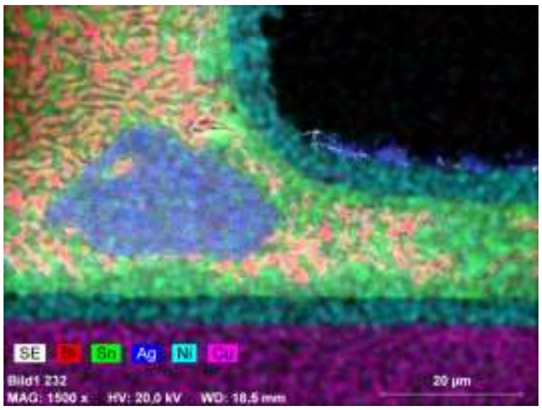

Fig. 9 Solder joint BiSnAg1 produced with BSA-01 profile and aged 168h at 150 °C (1500x)

Furthermore, increased growth of platelet-shaped Ag_3Sn phases (melting point is 460 °C) was observed in this variant, which in some cases reach the size of 50x70 µm (Fig. 10) and also locally bridge the solder gap between component and circuit board contact surfaces and can lead to increase of the remelting temperature of the final solder joint. In the meniscus area, the solder interconnection solidifies in the typical eutectic structure.

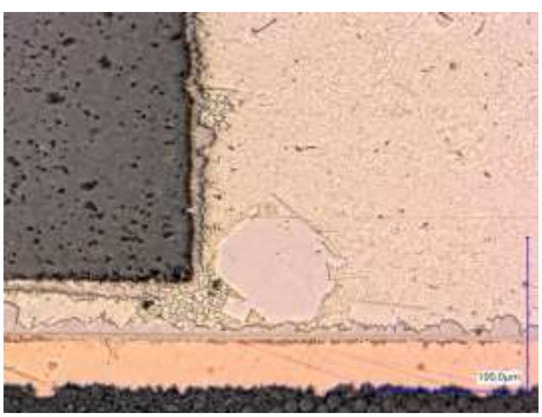

Fig. 10 Solder joint BiSnAg1 produced with BSA-01 profile and thermal aging 168h at 175 °C (1000x)

The inclusion of copper particles has significantly influenced the microstructure of the solder joint after thermal aging. An intermetallic phase Cu_6Sn_5 has been formed at the interface to the component and printed circuit board metallization. The phase thickness locally reaches a thickness of up to 15 µm. Due to a larger solder gap of the BiSnAg+Cu solder connection, however, no complete bridging was observed. In addition to the precipitation of Ag_3Sn phases, Cu_3Sn and Cu_6Sn_5 phases continued to grow around the included copper particles. Mostly complete transformation of copper particles into intermetallic phases was observed after aging at 175 °C for 168 h. Several Bi-crystal precipitations were observed both in the meniscus area and in the area of the solder gap (Fig. 11).

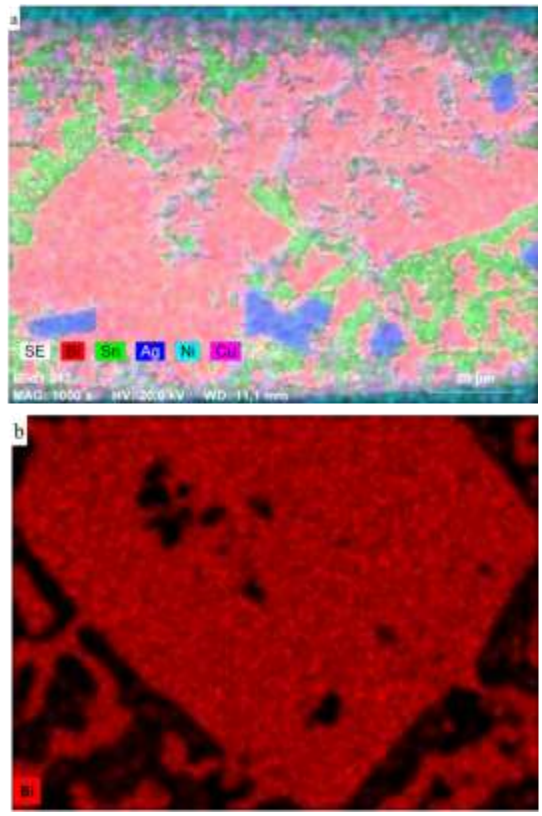

Fig. 11 Solder joint BiSnAg1+Cu after BSA-01 profile and thermal aging 168h at 150 °C: solder gap area (a) / meniscus area (b); (1000x / 2000x)

A complete local bridging of the solder gap by these crystals, which border on the intermetallic Cu_6Sn_5 phase, could be observed. This leads to an increase in the remelting temperature of the solder joint up to the melting temperature of pure bismuth, which is around 271 °C. In addition to the phase precipitation and local bismuth crystals, the solder joint consists of larger areas with a typical eutectic structure of the base alloy. Copper particles / Cu_6Sn_5 phases were observed near or directly included in the bismuth crystals. Apparently, the copper particles act as initiation points for the nucleation of pure bismuth crystals.

IV. Investigation of the shear strength of the solder joints

After the various soldering processes and subsequent short-term thermal aging (10-30 min at 150 °C), the shear strength of the solder joints was examined using the example of the CR1206 component. The universal shear tester model Condor 70 from XYZtec was used for the investigation. The test was carried out destructively at a shear rate of 1 m/min.

When comparing the shear forces for different soldering profiles, a slight variation in the range of 10-15 % was found, this is within the range of the standard deviation (Fig. 12). The difference to the standard soldering profile for the eutectic solder alloy BiSnAg and a higher heat input during the soldering process can lead to a slight decrease in the shear strength of soldered joints, which is tolerable. The situation is similar when comparing the shearing forces after subsequent thermal aging (Fig. 13).

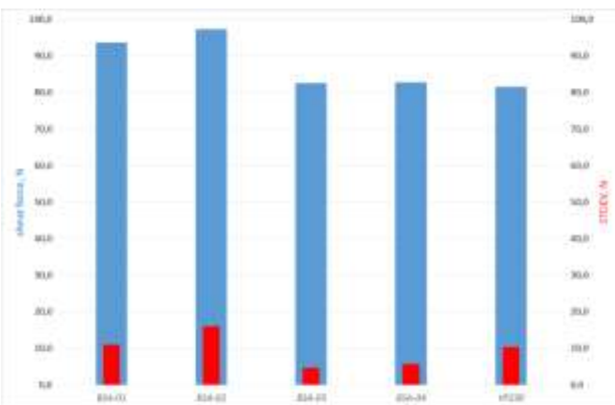

Fig. 12 Comparison of the shear strength of solder joints: with the variation of the soldering parameters

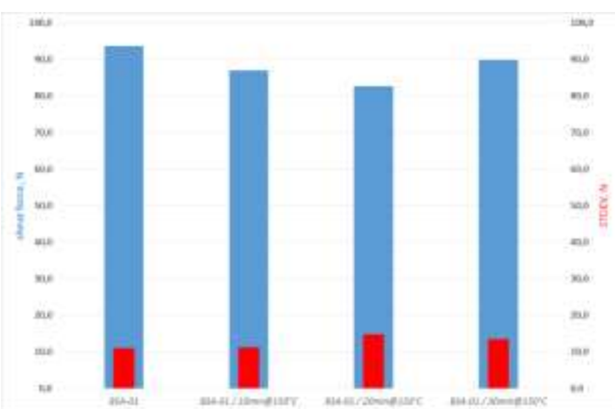

Fig. 13 Comparison of the shear strength of solder joints: with subsequent thermal aging

The value fluctuation is not significant and lies in the range of the standard deviation. The heating factor for additional thermal aging at 150 °C for 10, 20 and 30 minutes is 6.600, 12.200 and 18.800 K*s respectively. By adding the heating factor to the standard soldering profile BSA-01, you get comparable values for the heat input when the soldering time is extended and the peak temperature is increased (soldering profiles BSA-02, BSA-03, BSA-04 and VP230). This means that this subsequent storage does not have any negative impact on the mechanical strength of the solder interconnections.

When comparing solder interconnections BiSnAg and BiSnAg+Cu, a slight decrease in the shear strength values due to the addition of copper particles and soldering processes in the convection oven could be determined (Fig. 14). In contrast, during the soldering process in a vapor phase soldering system, a slight increase in the values for the soldered connections with the added copper particles was observed. In general, significantly higher standard deviations of the shear force values were observed for the BiSnAg+Cu solder joints. This can be explained by the changed spreading and wetting behavior of the modified solder paste. The solder spreads on the circuit board surface during the soldering process not so good and the wettability is limited by the added copper particles and a reduced proportion of flux.

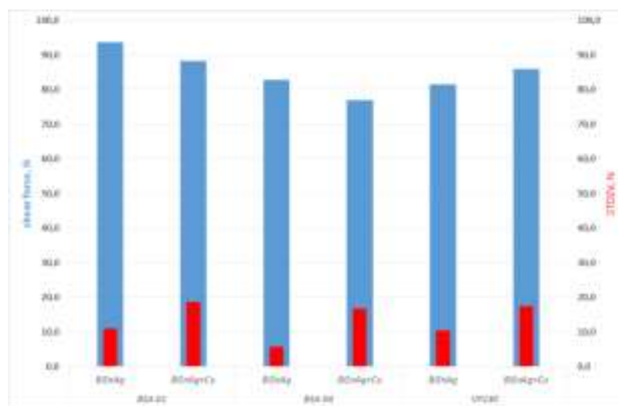

Fig. 14 Comparison of the shear strength of solder joints BiSnAg vs. BiSnAg+Cu

Furthermore, production tolerances in solder paste printing and assembly steps are not compensated by self-centering due to the surface tension of the melted solder. This automatically leads to a relatively frequent deviation in the geometry of the solder joint and, as a result, to a greater deviation in the mechanical strength values.

V. Conclusion

In this work, the influence of the heat input during the soldering process and subsequent thermal aging on the microstructure of the soldered joints BiSnAg and

BiSnAg+Cu was examined. The increased heat input during the extended soldering processes with increased peak temperature and aging at 150 °C for up to 30 minutes did not lead to any significant coarsening of the structure. The solder interconnection solidifies in the typical eutectic BiSn(Ag) structure. However, in the areas with a smaller solder volume, e.g. in the solder gap, a coarsening of the structure is possible even after the standard soldering profile. The higher heat input (heating factor) led to increased precipitation of Ag_3Sn and its transformation from a needle shape to a platelet shape.

Due to the addition of copper particles (10 % by volume in the examined samples), the reaction with the surrounding tin from the eutectic alloy during the soldering process and the formation of the intermetallic Cu_6Sn_5 phases were observed. The formation of Bi-crystals is accelerated by the local tin depletion of the base alloy. In addition, the copper particles can serve as initiation points for the local Bi-crystal growth. These effects were observed in this work. However, the relatively large solder gap could not be bridged with the intermetallic phase formations and the grown Bi crystals.

In order to accelerate this process, the duration of the subsequent thermal aging at 150 °C and at 175 °C was extended to 168 h. After this process, several Bi-crystals with the dimensions of approx. 50x70 µm were observed in the solder joint both in the meniscus and in the solder gap area. Together with the further transformation of copper into the intermetallic Cu_6Sn_5 phase and the further growth of this phase at the interfaces to printed circuit board and component metallization, several local bridging of the solder gap with these higher melting phases/precipitations than the base alloy could be observed. This leads to a local isothermal solidification of the solder joint and a corresponding increase in the remelting temperature.

The mechanical strength of the solder joints was examined by measuring shear forces. The higher thermal stress during the soldering process and the subsequent thermal aging at 150 °C did not lead to any significant reduction in mechanical strength. An increased deviation of measured values was observed for the solder joints with copper particles. This can be explained by the variation of the solder joint geometry due to limited wettability and spreading during the soldering process.

In further work, the dynamics of the transformation of the solder interconnections described above will be examined in more detail in order to optimize the process for possible practical use. The increase of the remelting temperature as the desired effect is to be determined on a model solder interconnection under defined test conditions [9], [10].

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