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## LEAD-FREE SOLDER JOINTS IN MICROELECTRONIC THICK FILM TECHNOLOGY

### POŁĄCZENIE BEZOŁOWIOWE W MIKROELEKTRONICZNEJ TECHNOLOGII GRUBOWARSTWOWEJ

The results of resistance and shear force measurements of several lead-free solder joints in thick film hybrid circuits are presented. The joints between lead-free thick film conductive layers and lead-free 1206 SMD components were prepared using Sn10In3.1Ag, Sn3.8Ag0.7Cu, Sn3.5Ag, Sn5Ag lead-free solders. The joints were prepared on Ag, PdAg, PtAg thick film solder pads. The solder joints were aged at 125°C for 1000 hours in order to estimate the solder joint properties in conditions corresponding to hybrid circuits exploitation in the engine compartment of an automobile. The electrical resistance was measured using the 4-wire method and the mechanical strength using a shear test. The microstructure of interfacial regions of the joints was tested with a scanning electron microscope. This research has shown that solder joints on Ag and AgPt layers exhibited the most stable properties, while joints on PdAg degraded in about 48 hours under test conditions.

W artykule przedstawiono wyniki badań hybrydowych bezołowiowych połączeń lutowanych w grubowarstwowym układach scalonych. Połączenia lutowane wykonano pomiędzy bezołowiowymi elementami 1206 przeznaczonymi do montażu powierzchniowego, a bezołowiowymi polami lutowniczymi w układzie grubowarstwowym wykonano stosując najbardziej popularne luty bezołowiowe. Badano rezystancję połączeń oraz siłę ścinającą połączenia. Pomiarów dokonano bezpośrednio po lutowaniu i po starzeniu połączeń w temperaturze 125°C. Połączenia lutowane wykonane lutami bezołowiowymi na srebrowych polach lutowniczych wykazują największą stabilność parametrów. Wytrzymałość mechaniczna połączeń lutowanych wykonanych na palladowo-srebrowych polach lutowniczych jest znacząco mniejsza, niż dla pozostałych połączeń.

### 1. Introduction

Since early 1990-ties, when the European Parliament decided to reduce the content of hazardous substances: lead, cadmium, mercury, and hexavalent chromium in electronic equipment, a lot of research of lead-free solder has been done. However, many properties of lead-free solders and lead-free solder joints have not yet been studied well enough. This concerns especially long-term reliability of solder joints [1]. Most research concerns the application of lead-free solders in printed circuit boards or flip chip technology. There is very little information about the use of lead-free solders in thick film hybrid circuits. Nowadays automotive industry is one of the main users of thick hybrid circuits. This application of lead-free solders may create some problems. Silver, palladium-silver and platinum-silver solder pads in thick film hybrid circuits are much more susceptible to the influence of solder than copper solder pads in printed circuit boards. Intermetallic phases formation at

the interface between solder and solder pad or solder and component contact may influence the resistance and the mechanical strength of the solder joint. These joint parameters may change during solder joint exploitation due to diffusion and intermetallic phases growth causing damage or improper operation of the electronic equipment. Some information on lead-free solder joints stability in thick film hybrid circuits is presented in [2].

The authors have undertaken wider and more comprehensive investigation of lead-free solder joints in thick film hybrid circuits aged at temperature 125°C. This is the temperature that can be reached by electronic equipment, e.g. in an automobile engine compartment.

### 2. Experimental procedure

Test pattern containing solder pads for 24 surface mounted 1206 components was designed as shown in Fig. 1.

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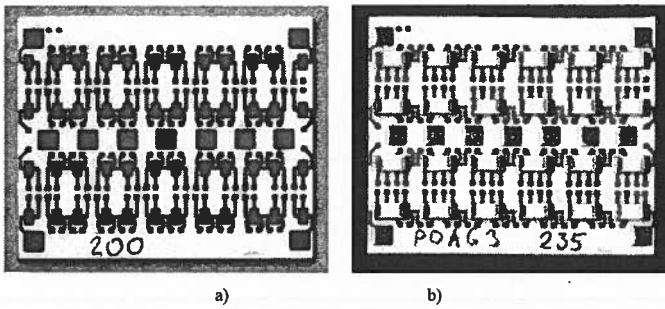


Fig. 1. Test pattern (a) and test 1206 components soldered to the solder pads (b)

The test pattern was printed with conductive pastes on alumina substrates containing 96%  $Al_2O_3$ . Lead-free Ag, PdAg and PtAg pastes, produced by the Institute of Electronic Materials Technology were applied. Pd content in PdAg paste was 20%, and Pt content in PtAg paste - 2%. Each solder pad was surrounded by a few contact pads for the joint resistance and the solder pad resistance measurements. Solder pads were covered with four lead-free solder pastes and one lead-containing paste for parameters comparison. 1206 lead-free jumpers, the contact cross section of which is presented in Fig. 2 were placed on the solder pads.

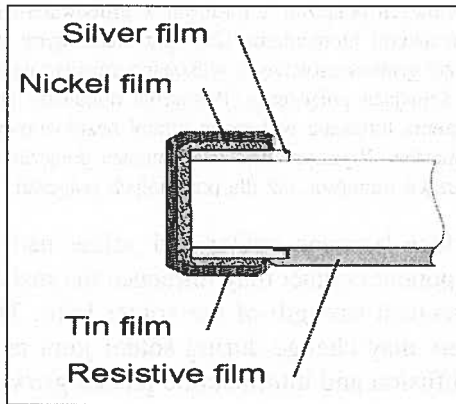


Fig. 2. Cross section of component contact

Reflow soldering was done with the use of BTU International convection tunnel oven type VIP70A at Tele- and Radio research Institute in Warsaw, with the solder profiles as shown in Fig. 3.

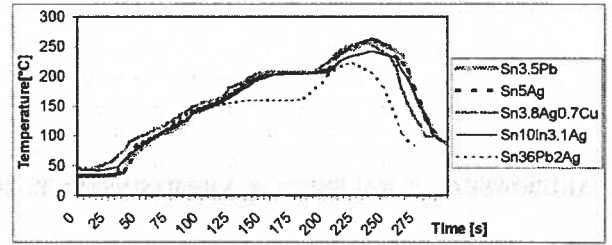


Fig. 3. Soldering temperature profiles

Tin was the main component of the solders under investigation. The solders composition and melting temperature were varied. The composition of applied solders, melting temperatures and soldering temperatures are presented in Table 1.

Resistance of solder joints was measured with Keithley multimeter M2001. Four-wire method of resistance measurement was applied. Special adoption, consisting in increasing measurement current from about 10 mA to 1 A, was necessary to avoid electromagnetic interference and make low resistance measurement possible. Resistance of each solder joint was measured separately. Each point of the resistance diagram represents mean resistance value of 48 solder joints.

Shear test was performed to measure the solder joints mechanical strength. Shear force was applied to the body of 1206 components parallel to the substrate. Both solder joints were sheared at once, and then the shear force was recorded. Each point at the diagram represents the mean value of 24 shear force measurements.

The joints after the shear test were observed using an optical microscope. This observation allowed identifying several kinds of damages of solder joints, shown in Figure 4. To each observed damage, the number corresponding to the place of appearance of the damage was attributed. The damage of the solder joint takes place in the weakest part of this joint, thus it indicates the exact place of solder joint degradation. The damage kind changes are related to structure evolution of the joint elements during aging.

Pictures of solder joints fractures were recorded with the use of scanning electron microscopy.

TABLE 1

Melting temperatures and reflow temperatures of applied solders

Solder Composition	Sn36Pb2Ag	Sn10In3.1Ag	Sn3.8Ag0.7Cu	Sn3.5Ag	Sn5Ag
Solder Type	Koki Se48-M955	Ind 254	Ind 217	Ind 121	Ind 132
Melting Temperature [°C]	181	205	217	221	$T_L = 240$ $T_S = 221$
Reflow Temperature [°C]	215	235	247	251	255

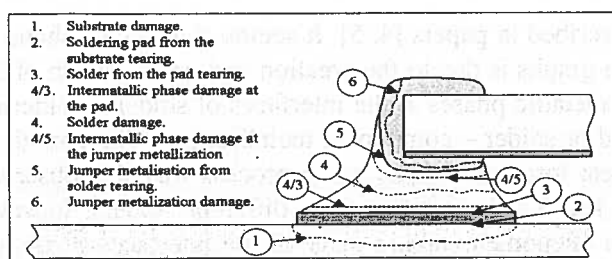


Fig. 4. Damage kinds of solder joint

### 3. Results

The resistance measurements have shown that the lead-free solder joints resistance on platinum-silver and silver solder pads is close to that made with tin-lead solder, while for palladium-silver solder pads the lead-free solder joints resistance is considerably lower.

Solder joints resistance versus aging time for various solders and solder pads are presented in Fig. 5a-c. For all tested lead-free solders on Ag solder pads (Fig. 5a) the solder joint resistance is similar. The resistance increases during the first 250 hours, and then stabilizes at the level about  $575\mu\Omega$ . Only the reference Sn36Pb2Ag solder joints do not reach stabilization. Solder joints resistance for joints on palladium-silver pads (Fig. 5b) shows the dependence on soldering temperature. The initial resistance growth is higher for solders reflowed at lower temperatures, i.e. for Sn36Pb2Ag and Sn10In3.1Ag. These solders have also higher stable resistances during further aging. The joint resistance of the remaining Sn3.8Cu0.7Ag, Sn3.5Ag and Sn5Ag solders is stable until 500 hours, when a slight decrease takes place. The joint resistance on PtAg solder pads for all investigated solders is similar. The resistance increases for the first 250 hours, reaching  $650\mu\Omega$ , and then slightly decreases. For all tested solders, except the Sn3.8Cu0.7Ag, Sn3.5Ag and Sn5Ag on PdAg solder pads, the resistance increase occurs, which could probably result from the intermetallic phases creation. During the soldering process the  $Ni_3Sn_4$  phase is formed at the interface between solder and resistor contact. Silver from solder pad and nickel from resistor contact dissolve in the solder during the soldering process. After crystallization these components create intermetallic phases –  $Ag_3Sn$  at the solder-solder pad interface and  $Ni_3Sn_4$  at the resistor contact-solder interface. Further Intermetallic phases growth takes place in the solid state. The intermetallic phases growth rate in the solid state is limited by components diffusion through the intermetallic phase layer.

It is assumed, that the growth of  $Ni_3Sn_4$ , with resistivity  $28.5\mu\Omega\text{cm}$ , is high compared to Ni ( $7.8\mu\Omega\text{cm}$ ) or solders ( $10\text{--}15\mu\Omega\text{cm}$ ), it has stronger influence on solder joint resistance than  $Ag_3Sn$ , whose resistivity is equal to  $7.7\mu\Omega\text{cm}$ . The resistance growth was not observed in case of Sn3.8Cu0.7Ag, Sn3.5Ag and Sn5Ag solders on PdAg solder pads (Fig. 5b). Probably during reflowing of these solders at relatively high temperature, some amount of palladium from solder pad dissolved in solder and blocked intermetallic phases formation during aging in the solid state. For Sn36Pb2Ag and Sn10In3.1Ag on PdAg solder pads (Fig. 5b) the reflow temperature was insufficient to cause quick enough dissolving of palladium in the solder, therefore intermetallic phase layers were created in the solid state at the initial period of aging. The long term solder joints resistance decrease for palladium-silver and platinum silver solder pads is a noteworthy phenomenon. The cause of such a decrease seems to be the solder or intermetallic grains growth during recrystallisation and  $Ni_3Sn_4$  dissolution in solder. Resistance decrease was observed during long term aging in [3]. Resistance of solder joints made on nickel-plated copper solder pads was under investigation. At that stage of investigation the authors could not explain the resistance decrease during aging.

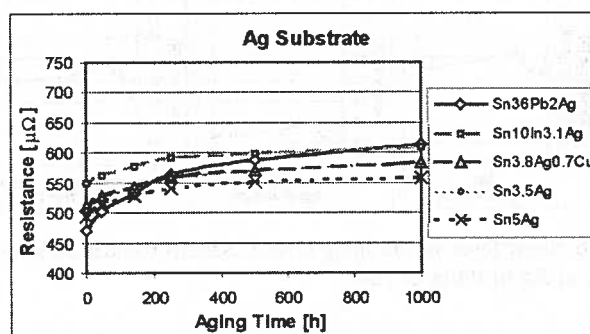


Fig. 5a. Resistance of various solder joints on Ag solders pads

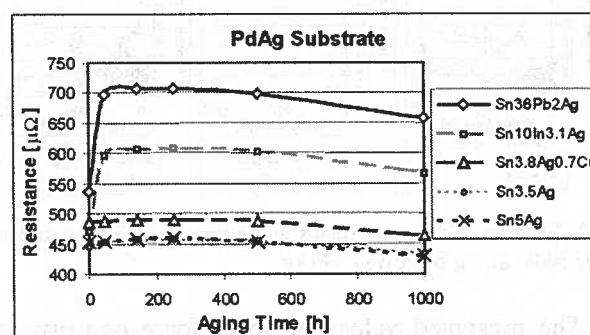


Fig. 5b. Resistance of various solder joints on PdAg solders pads

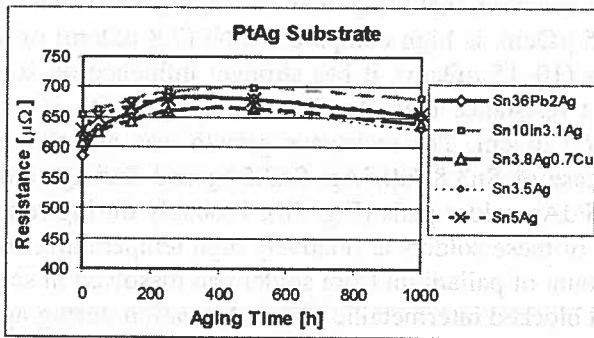


Fig. 5c. Resistance of various solder joints on PtAg solder pads

A strong correlation between the solder pad material and the shear force was revealed. For all tested lead-free solders the solder joints on Ag and PtAg solder pads exhibited stable and relatively high shear force compared with the tin-lead-silver solder. On the other hand, the lead-free solder joints on PdAg solder pads have shown considerably lower shear force. The Sn3.5Ag solder was chosen as an example for the results presentations. The other tested lead-free solders behaved analogously. The shear force and the number of damages of individual type for solder joints made with Sn3.5Ag solder are shown in Figures 6a)-c) and 7a)-c).

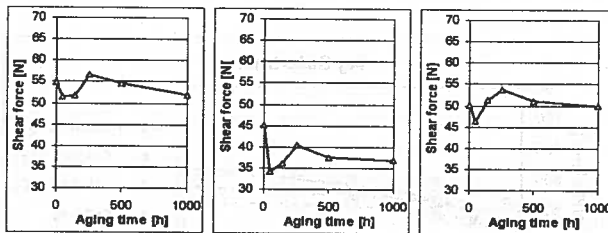


Fig. 6. Shear force versus aging time of Sn3.5Ag solder on solder pads: a) Ag b) PdAg c) PtAg

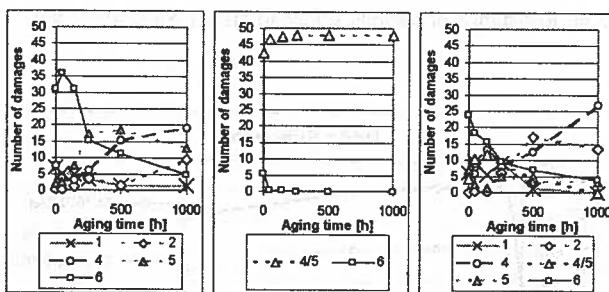


Fig. 7. Number of damages versus aging time of Sn3.5Ag solder on solder pads: a) Ag b) PdAg c) PtAg

The presented values of shear force concern both connections of one component. For all the tested solder pads shear force for Sn3.5Ag solder decreases in the initial aging period, then reaches local maximum and later decreases until stabilization. Similar changes of in the lead-free solder joints mechanical properties were

described in papers [4, 5]. It seems, that such a shape of the graphs is due to the creation and grain growth of intermetallic phases at the interfaces of solder – soldering pad or solder – component metallization. The growth of shear force during the aging process was also observed in [6]. This paper concerns different solders, however the phenomena taking place at the interfaces of phases can be similar. It is worth to mention that the shear force for the lead-free solder joints on palladium-silver solder pads is considerably smaller than on silver and platinum-silver solder pads. Till now as the lead containing solders have been applied, the palladium-silver solder pads have been regarded as the most appropriate because of its the highest resistance to dissolving in solder of the conductive materials used in thick film hybrid circuits. As it is seen from microscopic observation of the shown solder joint (Figure 7a)-c)), some kinds of damages classified according to Fig. 5 do not appear. Damage no.3 (tearing the solder from solder pad) does not occur, which proves good wettability of the applied layers by the lead-free solders and good adhesion of solders to these layers. One should notice that the resistance of solder joints made on palladium-silver (20% Pd) solder pads is considerably lower resistance than joints made on silver or platinum-silver (2% Pt) solder pads. The investigation revealed the strong dependence between the shear force and the number of damages of definite kind. For palladium-silver solder pads (Figure 7b) the damage No. 4/5 is predominant (damage of intermetallic phase at the component metallization), however for silver (Fig. 7a) and platinum-silver (Fig. 7c) solder pads many kinds of damages coexist without domination of any of them. For silver solder pads the damage No. 4/5 does not occur, for platinum-silver (2% Pt) the addition of platinum causes appearance of damages No. 4/5. Addition of 20% palladium to the material of the soldering pad causes considerable low shear strength of the interface between solder and component metallization (damage No. 4/5), which causes a significant shear force decrease. The damage of the joints observed on palladium-silver solder pads occurred at the solder and the component metallization interface, which proves that the material of solder pad influences the component metallization interface.

The fractures of solder joints were made to explain the solder joints resistance and shear force behavior. The fractures were observed with the use of a scanning electron microscope. Solder joints made with Sn3.5Ag were chosen for fracture investigation. SEM pictures of bare solder pad fracture and solder pads covered with solder fractures are presented in Fig. 8a and Fig. 8b. Bare solder pad fracture has homogenous coarse-grain structure with some small pores. During the soldering process the



upper part of the solder pad (at the solder) changed its structure into a fine-grained one. The bottom part of the solder pad (at the substrate) did not change (Fig. 8b). After annealing for 48 hours the grain dimensions of intermetallic phase  $Ag_3Sn$  in the upper part of the solder pad increased. Pores perpendicular to the substrate appeared in the bottom part of the solder pad. Oval-shaped structures, probably  $Ag_3Sn$ , were created in the solder at the solder-solder pad interface (Fig. 8c). After 500 hours of annealing the grain dimensions in the upper part of solder pads increased considerably. The number of pores in the bottom part of the solder pad increased, too. Oval-shaped structures at the solder-solder pad interface were grown (Fig. 8d). It seems that the fine-grain structure at the solder-solder pad interface was created of silver from solder pad dissolved in molten solder. It is very probable that this layer is built of  $Ag_3Sn$  or that it is  $Ag_3Sn$  rich. Silver diffusion from the solder pad to the solder takes place during aging. The result of silver diffusion is grain growth and formation of pores in the solder pad.

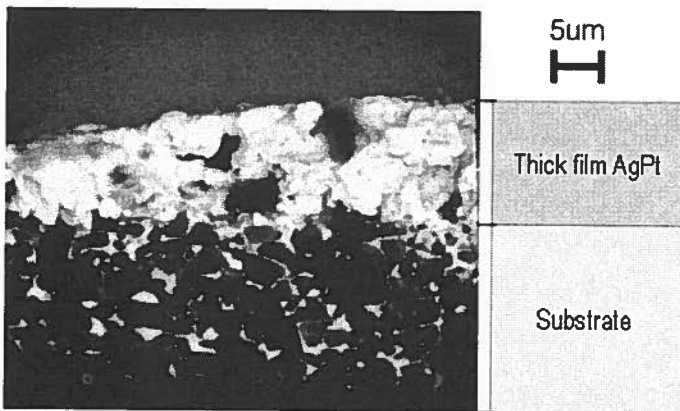


Fig. 8a. Thick film layer fracture

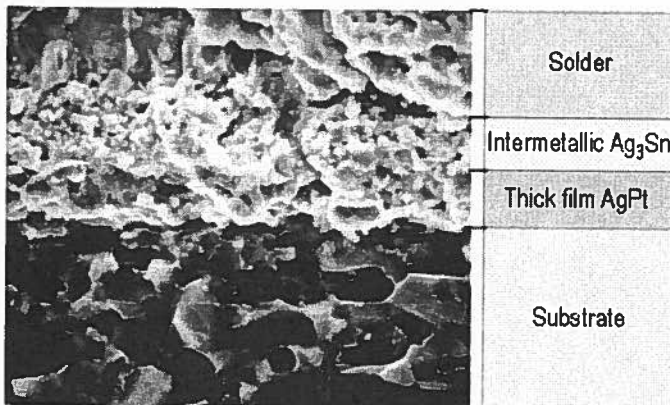


Fig. 8b. Solder joint fracture just after soldering

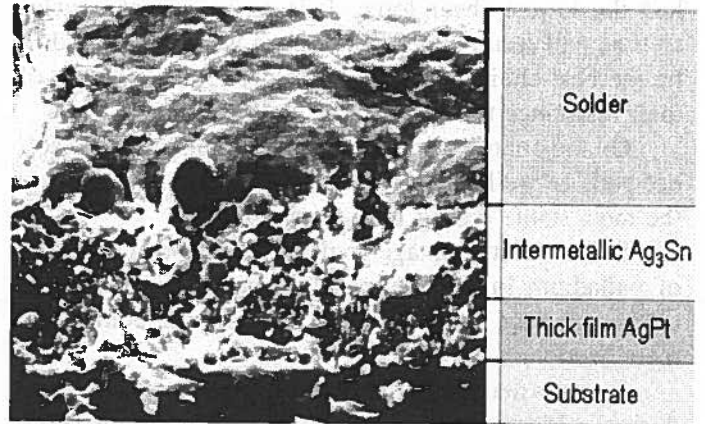


Fig. 8c. Solder joint fracture after 48h aging

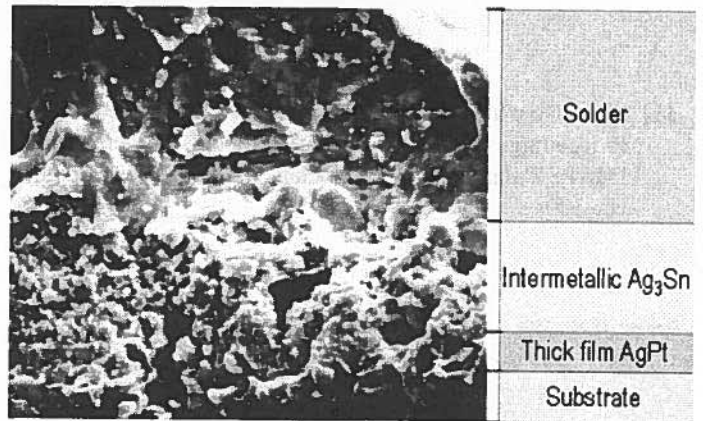


Fig. 8d. Solder joint fracture after 500h aging

Basing on these results the authors suppose that in case of all tested solder joints except Sn3.5Ag, Sn5Ag and Sn3.8Ag0.7Cu on PdAg solder pads, the intermetallic growth during aging took place. The presence of intermetallic phases probably provides high and stable shear force, while their insufficient thickness results in low and unstable mechanical properties.

The authors intend to perform investigation of the chemical composition profile vertically to the substrate surface to confirm the above suggestions. Crystallographic structure investigations in various parts of the solder joint might confirm the intermetallic phases creation.

#### 4. Conclusions

Lead-free solder joints produced using three solder pads materials and four solders in thick film hybrid circuits were investigated, including solder joint resistance measurement, shear test, and SEM photographs observation.

These properties, concerning especially the shear force, vary during annealing in an unexpected way. Lead-free solder joints on palladium silver solder pads

had the lowest shear force. It is an important conclusion as palladium-silver solder pads were considered to be the best choice for tin-lead solder joints, because of their resistance to dissolving in SnPb solder.

On the contrary, lead-free solder joints on silver solder pads as well as on platinum-silver solder pads were the most stable during long term aging.

Solder joints damage analysis showed that presence of palladium in thick film solder pads causes damage of the interface between the solder and the component metallization.

It seems that phenomena taking place in solder joints during soldering and aging of thick film circuits need further detailed investigation including chemical composition measurement and a crystallographic investigations.

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