„Lead-free solder materials- state of art and perspectives for the future"

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Lead was until recently a widely used element in many components of the electronics industry. It appears in the solder material, coatings soldered on printed circuit boards, pins and ends of boards. On one hand, the commonness of the electronic equipment which accompanies almost every aspect of our lives (~ 8 million tones of waste per year in EU countries) and on the other hand, great dispersion of lead within it, made Pb recovery and recycling impossible. As a result of wastes, corrosion toxic lead compounds were passing into groundwater and contributing to environmental pollution. Harmful effect of lead on human health is well known - its accumulation in the body causes disorders in the nervous and reproductive systems, the delays in neurological and physical development, anemia and hypertension.

In the 90's of the last century Japan and the U.S. began research on the replacements of typical PbSn solders. Among the countries of the European Union breakthrough came about 10 years later, along with two directives of the European Parliament and the Council: RoHS (2002/95/EC) *On the restriction of the use of Certain Hazardous Substances in electric and electronic equipment* and WEEE (2002/96/WE) *On waste electric and electronic equipment* [1,2]. In 2001 started COST Action 531 Lead-free solder materials [3] gathering 45 scientists from 19 European countries, 4 from Institute of Metallurgy and Materials Science Polish Academy of Sciences (IMMS PAS) who began to work on replacements for conventional PbSn solder. As a result critically assessed thermodynamic parameters collected either from the literature or provided by the experiments within the project gave a set of 53 binary and 20 ternary equilibrium phase diagrams. Eleven elements (Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn, Zn) meaningful for soldering are the scope of the created database [4]. Moreover, valuable compilation of properties of the so-called SACs (solders of near eutectic composition of SnAgCu) and joints was created in the frame of COST531 [5].

The replacement of the PbSn solder by the Pb-free one brought new reliability problems to overcome. They raised mostly due to the fact that tin is the main constituent of such joints. In general tin can be alloyed with noble metals like Au, Ag or Cu and also Zn, Bi, In, Sb and Ge. Tin reacts with other components of the joint forming the intermetallic phases (IPs) which is not an issue in a case of PbSn. The microstructure of these IPs is different, taking the shape of the plates (Ag_3Sn), whiskers (Sn) or rods (Cu_6Sn_5) widely described in the literature [6].

What becomes even more problematic in a case of the whiskers is the fact that they are formed not during the production but storage and service.

Currently, among other typical lead-free solders such as: SnCu, SnAg, SnZn, SnBi, SnZnBi, the SACs are the best candidates to replace PbSn. The melting temperature of the SnAgCu eutectic is significantly higher (217 ^{o}C) than conventional one (183 ^{o}C) and thus the reflow temperature rises up to about 240 ^{o}C. The new solder material also makes soldering time longer. As a result problems appear with ply separation of the laminates or greater oxidation of the solders. So called "temperature window" is much smaller in the case of lead-free soldering than for PbSn. Moreover, notably higher surface tension of the lead-free solders in comparison to PbSn which results in worse wettability [7-9]. At the moment, an intensive research in IMIM PAS is focused on the lead-free solder material containing: Sn, Ag, Cu and Bi.

Although, there are no restrictions to the high-temperature solders, the awareness of the harmful effect of lead makes it only a matter of time. The only one replacement for high-temperature solder Pb95Sn5 is Au70Sn30 with eutectics melting temperature of 280 ^{o}C. However, the cost of such solder together with its poor reflow behavior seem to be another challenge to overcome. Therefore, next COST Action was proposed - MP0602: *Advanced Solder Materials for High-Temperature Application*- their nature, design, process and control in a multiscale domain [10]. It started in 2006 and gathered European researchers from universities, research institutions and industrial research centers whose field of interest falls for new high-temperature Pb-free solders. Several combinations are under consideration. Hypo-eutectic Bi-Ag alloys are one of the most promising because of their liquidus temperature, good mechanical properties close to Pb-based solders and price. Other possible solders are those based on Sb-Sn, Au-Sb-Sn and Zn-Al eutectic alloyed with Mg, Ga, Ge, Sn or Bi. The aim is to compile a set of databases containing information on phase diagrams, thermodynamic, structural, physical, chemical, electrical, mechanical and process related properties of possible solders and corresponding joint materials.

IMIM PAS took part also in another project called *European Lead-Free Soldering Network* (ELFNET) gathering 36 partners from 19 European countries: leading electronic companies such as Philips, Siemens, Bosch, Hewlett Packard etc. and researchers from all over the Europe [11]. The aim of ELFNET was to coordinate, integrate and optimize research which would allow electronics producers to introduce lead-free technology. Also the strong cooperation between both mentioned COST Actions and ELFNET allows to compare and improve gathered knowledge and results.

Main scientific interest in the IMIM PAS is connected with the development of the equilibrium phase diagrams of special interest such as Sn-Ag-Cu or Sn-Ag-Cu-Bi (Fig. 1), measurements of the wetting properties of the solder alloys (Fig. 2) and microstructure and mechanical characteristics of the lead-free interconnections. They are all performed under projects sponsored by Ministry of Science and Higher Education as well as Operational Programme-Innovative Economy, projects: *Reliability improvement of the lead-free joints in the electronic devices (Pb-free), Advanced materials and their technology (ZAMAT) – New environment friendly multicomponent Cd and Pb-free solders on the basis of Zn-Al and Zn-Sn systems with Ag, Sn, Cu, In additions (task 4.3).*

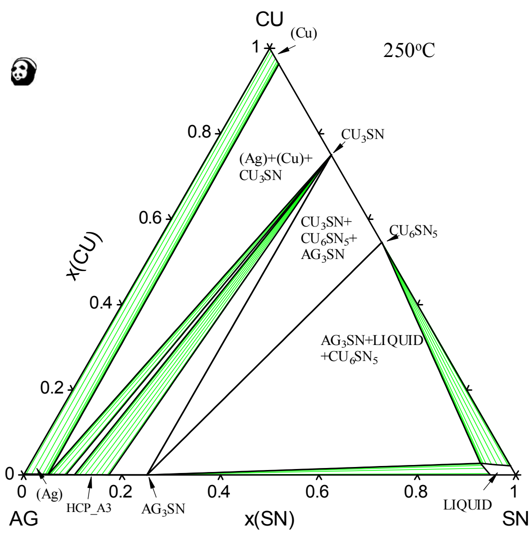

Fig. 1. Isothermal cross-section of Ag-Cu-Sn system at 250 °C calculated based on the thermodynamic data base of COST 531 ver. 3 (unpublished assessment by Gisby i Dinsdale.)

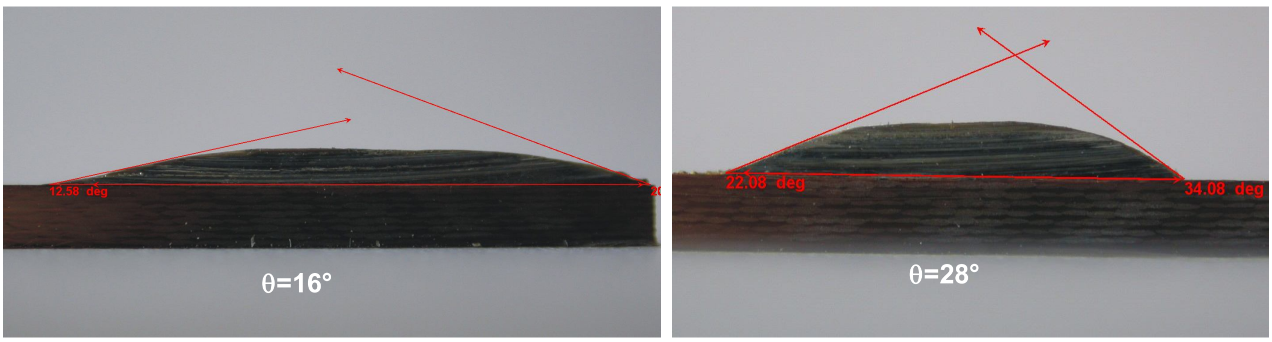

Fig. 2. Wetting angle of SAC 305 (a) and SAC X0307 (b) both on gold covered laminate.

Since couple of years the intensive work on physical properties (density of solids and liquid, liquid surface tension, viscosity, contact angles, resistivity, linear expansion, melting temperature) of the lead-free solders has been performed in IMMS PAS. Under studies are among others SACs with higher amount of Cu and Ag and with Bi, In, Sb additions, alloys based on the eutectics: BiAg with Sn, Zn, Cu, Ni and SnZn with In, Ag, Cu, Li [12,13]. The SURDAT free database (Fig. 2b) is one of the achievements in this field [14,15]. It was developed in IMMS PAS (2002-2005) with partial funding of the Ministry of Science and Higher Education and in the frame of the international network *Associate Committee of phase diagrams and thermodynamics: Poland, Czech Republic, Bulgaria, Hungary, Slovakia, Romania, S* ... *tene* ... ns experimental data of surf ... mol ... s. The database consists of ... he ap ... tion and Butler method of ... g an ... and using the program.

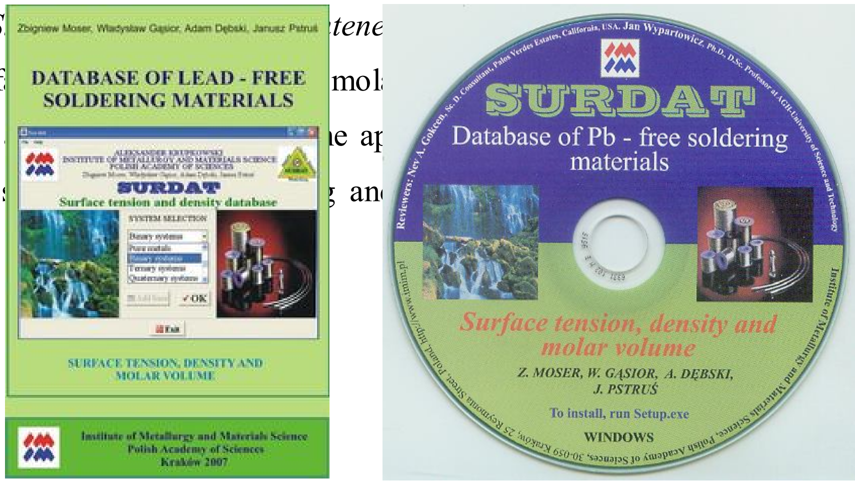

Fig. 3. SURDAT database which contains experimental data of surface tension, density and molar volume for pure metals and alloys.

IMIM PAS cooperates very effectively with *Fideltronik IMEL* company – leading Polish manufacturer of electronics. The transfer of knowledge and experience from the both sides results in solving current production problems and allows for better understanding of the problems coming up with lead-free technology such as the black pad effect. Figure 4a shows the printed circuit board where the problem with Pb-free soldering occurred. Figures 4b and 4c are SEM microphotographs showing the microstructure of the defected area in details. Finally Fig. 4d is the cross-section of the soldered area showing the lack of solderability of the "black surface" to the SAC alloy. One of the most commonly referred explanation of this phenomenon is corrosion in immersion Au bath or immersion gold hyperactivity but there are more potential sources of the problem as described in [16].

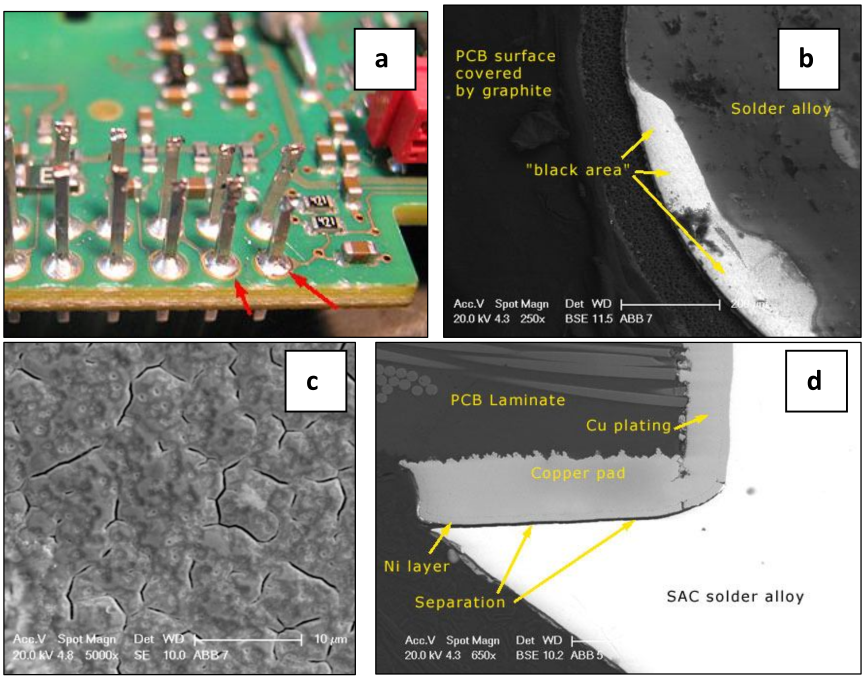

Fig. 4. Example of common PCB manufacturer problem – *black pad* effect [16]. The surface is black with low magnification visual observation (a). Observations using scanning electron microscope (IMIM PAS) of the problematic area (b) under higher magnification shows typical "cracked mud" appearance (c). Cross-section of this area (d) demonstrates lack of solderability of the "black surface" to the SAC alloy. Courtesy of Fideltronik SA.

Reliable PbSn replacements is not the only issue that emerged in the field of modern materials joining. There is a steady increase in the number of components and systems operating at temperatures above 350 °C, especially in circuits built on silicon carbide and III-V compound semiconductors. They are used in jet engines, nuclear reactors, geothermal walls, automotive electronics, industrial robots, space electronics. Moreover, the progressive miniaturization in electronic packaging increase the specific load of contacts due to heat dissipation. Heat-dissipating elements such as chip resistors and resistant heating elements cannot be connected with the lead using a conventional soldering, since the maximum operating temperature solder is about 60-100 °C lower than the soldering temperature (typically 220-260 °C). Existing gap can be successfully filled by using low-temperature diffusion soldering process. As it was already mentioned, the intermetallic phases are undesired during conventional soldering except for a thin and continuous IP layer which is an important requirement for good wetting and bonding. On the contrary, during diffusion soldering their growth is totally controlled and at the end of joining process one or more intermetallics completely fill the joined area. In this way the interconnection has a high thermal stability as it reflects the properties of the intermetallic compound. [17,18].

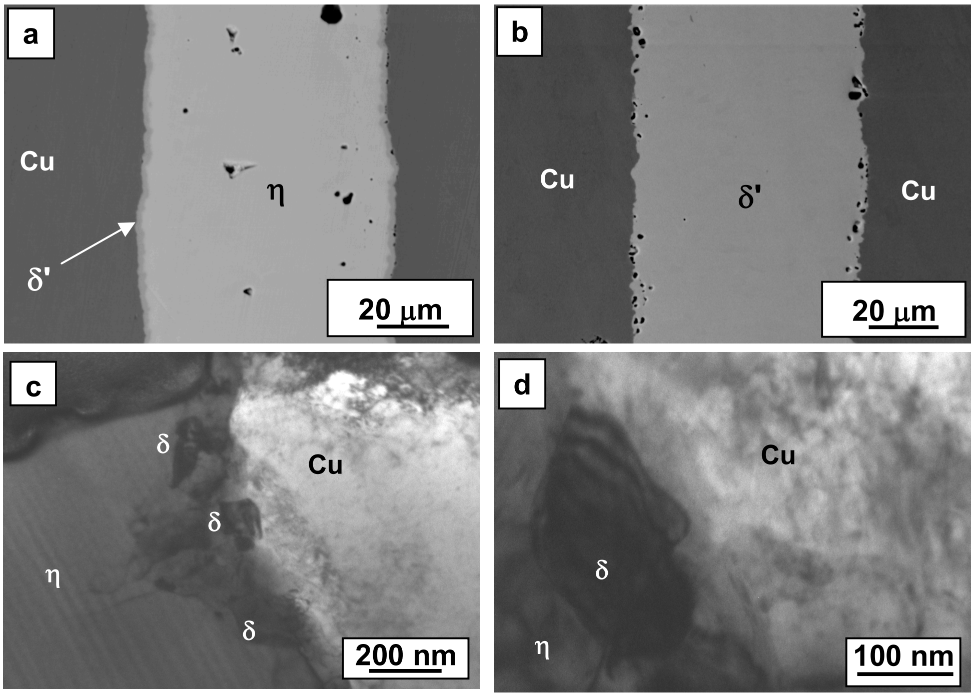

Fig. 5. SEM images of Cu/In-48Sn/Cu interconnections showing different microstructures in dependence on the temperature and time of annealing: 200 °C/3 days (a) and 300 °C/3 days (b). TEM images showing the Cu/η interface decorated with the small precipitates of δ′ phase (c, d).

In the recent years IMMS PAS studied several type of diffusion soldered interconnections such as Cu/In-48Sn/Cu, Cu/In-22Bi/Cu, Ag/Sn/Ag or Ag/In/Ag [19-22]. Figure 5 represents an example of diffusion-soldered Cu/In-48Sn/Cu joint where either η[$Cu_6(Sn,In)_5$] or δ′[$Cu_{41}(Sn,In)_{11}$] fulfilled the joined area.

References:

[1] Directive 2002/95/EC of the European Parlament and of the Council, 27th of January 2003, *on the restriction of the use of certain hazardous substances in electric al and electronic equipment (RoHS).* Official Journal of the European Union, L 37/19, 12.2.2003.

[2] Directive 2002/96/EC of the European Parlament and of the Council, 27th of January 2003, *on waste electric and electronic equipment (WEEE)*. Official Journal of the European Union, L 37/24, 12.2.2003.

[3] http://www.univie.ac.at/cost531

[4] COST Action 531 - *Atlas of Phase Diagrams for lead-free soldering*, compiled by A. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, J. Vizdal, COST Office 2008

[5] ELFNET COST Action 531 – *Handbook of properties of SAC solders and joints*, compiled by C. Schmetterer, H. Ipser, J. Pearce, COST Office 2008

[6] K.N. Tu, *Solder joint technology: Materials, Properties and Reliability*, Springer 2007, New York, USA

[7] *Lead-free electronics*, edited by S. Ganesan, M. Pecht, John Wiley & Sons 2006, Hoboken, New Jersey, USA

[8] J.W. Evans, D. Kwon, J.Y. Evans, *A Guide to Lead-Free Solders: Physical Metallurgy and Reliability*, Springer 2007, London, UK

[9] Elektronik Plus (1) 2006, poradnik dla producentów i dystrybutorów elektroniki

[10] http://cost602.ipm.cz

[11] http://www.europeanleadfree.net

[12] Z. Moser, W. Gasior, K. Bukat, J. Pstrus´ , R. Kisiel, J. Sitek, K. Ishida and I. Ohnuma: *Pb-Free Solders: Part III. Wettability Testing of Sn-Ag-Cu-Bi Alloys with Sb Additions*, J. Phase Equilibria and Diffusion 28 (2007) 433-438.

[13] P. Fima, W. Gąsior, A. Sypień, Z. Moser, *Wetting of Cu by Bi-Ag based alloys with Sn and Zn additions.* J. Mater. Sci. 45 (2010) 4339-4344.

[14] http://imim.pl/baza-danych-surdat

[15] Z. Moser, W. Gąsior, A. Dębski, J. Pstruś: *SURDAT- Database of Lead-Free Soldering Materials*, Polish Academy of Sciences, Institute of Metallurgy and Materials Science, OREKOP 2007, Kraków.

[16] G. Milad, J. Martin: *Electroless Nickel/Immersion Gold, Solderability and Solder Joint Reliability as Functions of Process Control*, October 1, 2000. http://www.circuitree.com

[17] D.M. Jacobson, G. Humpston: *Diffusion soldering,* Sold. Surf. Mount Technol. 10 (1992) 27-32.

[18] D.M. Jacobson, S.P.S. Sangha: *Novel applications of diffusion soldering,* Sold. Surf. Mount Technol. 23 (1996) 12-15.

[19] Zięba P., Wojewoda J.: *Application of diffusion soldering in lead-free interconnection technology* in: *Recent Research Developments in Materials Science 4*, Research Signpost, Kerala (2003) 261-282.

[20] J. Wojewoda: *Solid state transformations in Cu/In-48Sn/Cu diffusion soldered interconnections*, Solid State Phenomena 138 (2008) 165-174.

[21] J. Wojewoda-Budka, P. Zięba: *Formation and growth of intermetallic phases in diffusion soldered Cu/In-Bi/Cu interconnections*, Journal of Alloys and Compounds 476 (2009) 164-171.

[22] P. Skrzyniarz, J. Wojewoda-Budka, P. Zięba, A. Wierzbicka-Miernik: *Transmission electron microscopy of Ag/Sn/Ag interconnections*, Journal of Microscopy vol. 237 (3) (2010) 388-390.