MINING AND METALLURGY INSTITUTE BOR ISSN: 2334-8836
UDK: 622

UDK: 669.215/.22/.872/.65(045)=20 DOI:10.5937/MMEB1402117K

Ana Kostov, Aleksandra Milosavljević*, Radiša Todorović*, Lidija Gomidželović**

LEAD-FREE ALLOYS FOR ECOLOGICAL SOLDERS MANUFACTURING**

Abstract

Although the European Union's directive about environment protection as WEEE and RoHS have been carried out in 2003, led solders are still in used in Serbia. In the aim to respect the European and world directives and laws, it is necessary to reduce a quantity of toxic element and to establish lead and cadmium free solders in production. In this paper it was presented lead-free alloys, which are used for ecological solders manufacturing and various applications.
Keywords: *ecological solders, lead-free alloys, silver, gold, tin, indium.*

INTRODUCTION

On July 1, 2006 the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS) came into effect prohibiting the intentional addition of lead to most consumer electronics produced in the EU [1]. California is recently adopted a RoHS law [2] and China has a version as well. Manufacturers in the U.S. are received tax benefits by reducing the use of lead-based solder. With the Europeans WEEE Directive now mandating a phase out of lead in electronic soldering and Japan's efforts to do the same even sooner, lead-free is rapidly taking on momentum around the world.

Namely, the available evidence indicates that measures on the collection, treatment, recycling and disposal of waste electrical and electronic equipment (WEEE) as set out in Directive 2002/96/EC of 27 January 2003 of the European Parliament and of the Council on waste electrical and electronic equipment [1] are necessary to reduce the waste management problem linked to the heavy metals concerned and the flame retardants concerned. In spite of those measures, however, significant parts of WEEE will continue to be found in the current disposal routes. Even if WEEE were collected separately and submitted to recycling processes, its content of mercury, cadmium, lead and

* *Mining and Metallurgy Institute Bor, Zeleni bulevar 35, Bor, Serbia, e-mail: ana.kostov@irmbor.co.rs, aleksandra.milosavljevic@irmbor.co.rs, khurgan@ptt.rs, lgomidzelovic@yahoo.com*
** *The research presented in this paper has been done in the frame of the projects: "Development of ecological knowledge-based advanced materials and technologies for multifunctional application" No 34005 and "Modern multi-component metal systems and nanostructured materials with different functional properties" No 172037 financed by Ministry of Education, Science and Technological Development of the Republic of Serbia; as well as the project MIS ETC Code 1409, title "Promoting new ecologic filler alloys for soldering, based on the non-ferrous ore of the Romanian-Serbian cross-border area" within the Romania – Republic of Serbia IPA Cross-Border Cooperation Programme.*

chromium (VI) would be likely to pose risks to health or the environment.

Taking into account technical and economic feasibility, the most effective way of ensuring the significant reduction of risks to health and the environment relating to those substances which can achieve the chosen level of protection in the Community is the substitution of those substances in electrical and electronic equipment by safe or safer materials. Restricting the use of these hazardous substances is likely to enhance the possibilities and economic profitability of recycling of WEEE and decrease the negative health impact on workers in recycling plants.

Although the European Union's directive about environment protection as WEEE and RoHS have been carried out in 2003, led solders are still in used in Serbia. In the aim to respect the European and world directives and laws, it is necessary to reduce a quantity of toxic element and to establish lead and cadmium free solders in production.

In this paper it was presented lead-free alloys, which are used for ecological solders manufacturing and their various applications, which are optimal replacement materials for toxic ones. Those solders must have similar characteristics as standard solders and respect economical payable.

SOLDERING

Soldering is a process in which two or more metal items are joined together, by melting and flowing of a filler metal into the joint, the filler metal having a relatively low melting point. Soft soldering is characterized by the melting point of the filler metal, which is below 400°C [3]. The filler metal used in the process is called solder.

Soldering is distinguished from brazing by use of a lower melting-temperature filler metal; it is distinguished from welding by the base metals not being melted during the joining process. In a soldering process, heat is applied to the parts to be joined, causing the solder to melt and be drawn into the joint by capillary action and to bond to the materials to be joined by wetting action. After the metal cools, the resulting joints are not as strong as the base metal, but have adequate strength, electrical conductivity, and watertightness for many uses.

One of the most frequent applications of soldering is assembling electronic components to printed circuit boards. Another common application is making permanent but reversible connections between copper pipes in plumbing systems. Joints in sheet metal objects such as food cans, roof flashing, rain gutters and automobile radiators have also historically been soldered, and occasionally still are. Jewellery components are assembled and repaired by soldering. Small mechanical parts are often soldered as well. Soldering is also used to join lead came and copper foil in stained glass work. Soldering can also be used to affect a semi-permanent patch for a leak in a container cooking vessel.

Some examples of solder types and their applications are tin-lead (general purpose), tin-zinc for joining aluminium, and lead-silver for strength at higher than room temperature, cadmium-silver for strength at high temperatures, zinc-aluminium for aluminium and corrosion resistance, and tin-silver and tin-bismuth for electronics.

A solder is a fusible metal alloy with a melting point or melting range of 90 to 450°C, used in a process called soldering where it is melted to join metallic surfaces. It is especially useful in electronics and plumbing. Alloys that melt between 180 and 190°C are the most commonly used.

SOLDER ALLOYS

Tin-lead solders are commercially available with tin concentrations between 5% and 70% by weight. The greater the tin concentration, the greater the solder's tensile and shear strengths. At the retail level, the two most common alloys are 60/40 Sn/Pb and 63/37 Sn/Pb used principally in electrical work. The 63/37 ratio is notable in that it is a eutectic mixture, which means: it has the lowest melting point (183°C) of all the tin/lead alloys; and the melting point is truly a point - not a range.

At a eutectic composition, the liquid solder solidifies as a eutectic, which consists of fine grains of nearly pure lead and nearly pure tin phases, but in no way is it an intermetallic, since there are no tin-lead intermetallics, as can be seen from a tin-lead equilibrium diagram.

In plumbing, a higher proportion of lead was used. This had the advantage of making the alloy solidify more slowly, so that it could be wiped over the joint to ensure water tightness. Although lead water pipes were displaced by copper when the significance of lead poisoning began to be fully appreciated, lead solder was still used until the 1980's because it was thought that the amount of lead that could leach into water from the solder was negligible. Since even small amounts of lead have been found detrimental to health [4], lead in plumbing solder was replaced by copper or antimony, with silver often added, and the proportion of tin was increased.

Pure lead solder is known to go into solution causing big problems. Lead tin solder, however, is very stable and does not go into solution, even in land fill sites.

Hard solder, as used for brazing, is generally a copper-zinc or copper-silver alloy, and melts at higher temperatures.

In silversmithing or jewellery making, special hard solders are used that will pass assay. They contain a high proportion of the metal being soldered and lead is not used in these alloys. These solders also come in a variety of hardness, known as 'enamelling', 'hard', 'medium' and 'easy'.

Enamelling solder has a high melting point, close to that of the material itself, to prevent the joint desoldering during firing in the enamelling process. The remaining solder types are used in decreasing order of hardness during the process of making an item, to prevent a previously soldered seam or joint desoldering while soldering a new joint. Easy solder is also often used for repair work for the same reason. Flux or rouge is also used to prevent joints desoldering.

Silver solder is also used in manufacturing, when there is a need to join metal parts that cannot be welded. The alloys used for these purposes contain a high proportion of silver (up to 40%), and may also contain toxic cadmium.

Solder often comes pre-mixed with, or is used with, flux, a reducing agent designed to help remove impurities (specifically oxidized metals) from the points of contact to improve the electrical connection. For convenience, solder is often manufactured as a hollow tube and filled with flux. Most cold solder is soft enough to be rolled and packaged as a coil, making for a convenient and compact solder/flux package. The two principal types of flux are acid flux, used for metal mending, and rosin flux, used in electronics, where the corrosiveness of the vapours that arise when acid flux is heated could damage components. Due to concerns over atmospheric pollution and hazardous waste disposal, the electronics industry has been gradually shifting from rosin flux to water-soluble flux, which can be removed with deionised water and detergent, instead of hydrocarbon solvents.

LEAD-FREE SOLDER ALLOYS

Lead-free solders in commercial use may contain tin, copper, silver, bismuth, indium, zinc, antimony, and traces of other metals. Most lead-free replacements for conventional Sn60/Pb40 and Sn63/Pb37 solder have melting points from 5-20°C higher, though solders with much lower melting points are available.

Drop-in replacements for silkscreen with solder paste soldering operations are available. Minor modification to the solder pots (e.g. titanium liners and/or impellers) used in wave-soldering operations may be desired to reduce maintenance costs associated with the increased tin-scavenging effects of high tin solders. The properties of lead-free solders are not as thoroughly known and may therefore be considered less reliable in select applications, e.g. high reliability aerospace and life-critical medical. "Tin whiskers" were a problem with early electronic solders, and lead was initially added to the alloy in part to eliminate them. These problems are now considered negli-gible in modern alloys for most applications

However, solder containing lead is still used in high reliability military, aerospace-satellite and life-critical medical applications.

Different elements serve different roles in the solder alloy:

Silver provides mechanical strength, but has worse ductility than lead. In absence of lead, it improves resistance to fatigue from thermal cycles.

Copper lowers the melting point, improves resistance to thermal cycle fatigue, and improves wetting properties of the molten solder. It also slows down the rate of dissolution of copper from the board and part leads in the liquid solder.

Bismuth significantly lowers the melting point and improves wetability. In presence of sufficient lead and tin, bismuth forms crystals of Sn16Pb32Bi52 with melting point of only 95°C, which diffuses along the grain boundaries and may cause a joint failure at relatively low temperatures. A high-power part pre-tinned with an alloy of lead can therefore desolder under load when soldered with a bismuth-containing solder.

Indium lowers the melting point and improves ductility. In presence of lead it forms a ternary compound that undergoes phase change at 114°C.

Zinc lowers the melting point and is low-cost. However it is highly susceptible to corrosion and oxidation in air, therefore zinc-containing alloys are unsuitable for some purposes, e.g. wave soldering, and zinc-containing solder pastes have shorter shelf life than zinc-free.

Antimony is added to increase strength without affecting wetability.

The most attractive world lead-free alloys are so-called SAC alloys (Sn-Ag-Cu) [5]. This alloy is recommended for used by NEMI (National electronic Manufacturing Initiative) as possible replacement for lead-tin solder. SAC alloys possess relatively high temperature of melting (over 200°C) according to Sn63Pb37 (183°C), and because of that the attractive solution is adding of indium as the forth component in alloy (SIAC alloys).

Some of the alloys based on indium such as In-Sn, is mainly used in the process of cold soldering. The only faults of these alloys are high price of cost, but ductility, good lubricate and fatigue resistance are the qualities necessary for a good solders.

Likewise, the alloy which possesses some application in electronics is Sn-In-Ag alloy. The most popular is Indalloy 227 (Sn77,2In20Ag2,8), as well as Sn(71,5-91,9)In(4,8-25,9)Ag(2,6-3,3), with or without added forth element, according to investigations of Indium Corporation of America and Delphi Delco Electronic Systems.

So, the best solution is used the best properties of the both alloys Sn-In-Ag and Sn-Ag-Cu and made a new Sn-In-Ag-Cu alloy. In that case, indium content in alloy should not be high, in the aim to avoid partial melting of alloy, which is not good for practical application. The second reason is economical. High content of indium make higher price of solder. According to the above mention, the best results are reaching by the used solders with the follow content: 50-90% Sn, 10-30% In, till 10% Ag and till 2,5% Cu [6].

Besides alloys based on indium, it could be used solder alloys based on gold. This kind of alloys is especially used in multi-integrated electrical circuits with dense packages. Electronic industry is at the moment the biggest user of gold and its alloys Almost 90% of used gold and alloys based on gold are used as solders for electrical contacts at normal pressures and in vacuum.

These significant applications in electronics, gold is owing to its possibility to form low-temperature eutectic with the others elements which possess some kind of conductivity, such as In, Ga, Si, etc. [7].

Also, the phase diagrams of Au-In-Me types may play a significant role in understanding of development of microstructures at bound surface between solder materials based on indium and gold, and the base, as well as in predicting of properties and cohesion point that lead to design of potential bound surface.

Au-In-Sb-Ga and Au-In-Sb alloys (figures 1 and 2) belong to the group of possible solder materials with gold and indium.

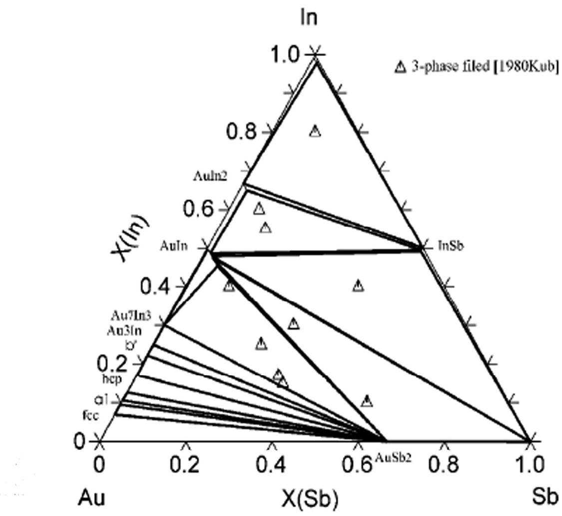

Fig. 1. *Isothermal cross-section of ternary system Au-In-Sb at 227 °C*

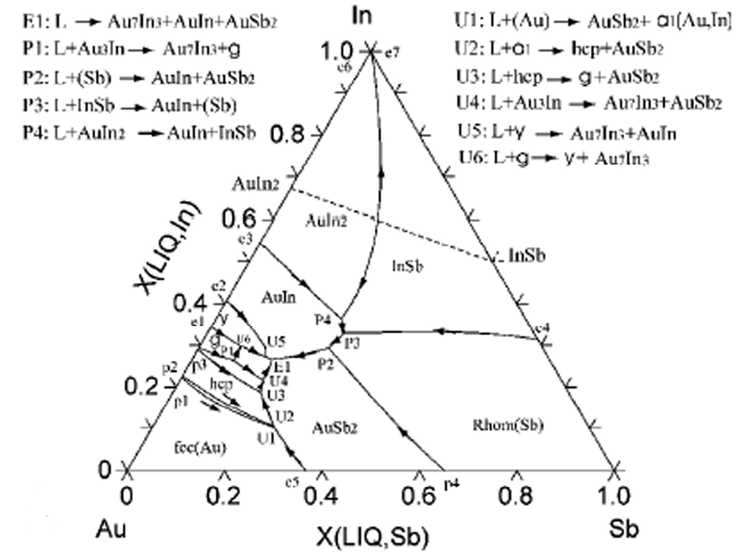

Fig. 2. *Calculated liquidus projection for ternary system Au-In-Sb*

CONCLUSIONS

The shown lead-free alloys for production of ecological solders are results of the investigation within project in the programme of researching in the field of technology developing – materials and chemical technologies during the first year of researching.

These alloys are possible to replacement toxic cadmium and lead in traditional solders. The ecological and energy efficient effects are achieved by the used of the shown alloys, as well as the better economical results, due to solder materials from abroad are replacement with the home-made products.

REFERENCES

[1] Official Journal of the European Union, Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment, p. 24.

[2] Information on http://www.dtsc.ca.gov/HazardousWaste/EWaste

[3] A. Rahn, The Basics of Soldering, John Wiley & Sons, (1993).

[4] PMID 2294437 (P, S, G, E, B), The Long-Term Effects of Exposure to Low Doses of Lead in Childhood, N. Engl. J. Med., 322 (2) (1990) 83.

[5] H. S. Liu, C. I. Liu, C. Wang, Z. P. Jin and K. Ishida, J. Electron. Mater., 32 (2003) 81.

[6] A. Milosavljevic, Thermodynamic Investigation and Structural Characterization of Alloys in Ag-In-Sn Ternary System, Master Thesis, University of Belgrade, Technical Faculty Bor, Serbia, (2006).

[7] L. Gomidzelovic, Comparative Thermodynamic Analysis and Phase Equilibrium Investigation in Au-In-Sb Ternary System, Master Thesis, University of Belgrade, Technical Faculty Bor, Serbia, (2007).