Properties and application of Zn-based solders

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ABSTRACT : *The aim of contribution is to summarize the knowledge about replacement of soldering alloys without use of lead, destined for higher application temperatures. Based on the study of properties and applicability, the Zn-based alloy was finally selected, which by its properties most approaches the Pb – based solders. This solder is further alloyed with different elements (for example Al, Sn, In, Mg, Ge and, Cu), in order to attain better wettability, strength and corrosion resistance. Following from the properties of Zn solders, this contribution is oriented to future application of these solders in common practice, as for example in electronic and automotive industry.*

KEYWORDS – *solders, Zn-based, higher application temperatures, properties, wettability, strength*

I. INTRODUCTION

Lead (Pb) was for a long time the main component of solders used extensively mainly in the electric and electronic devices. The research has shown, that of the five million tons of lead consumed on our planet per year, around 81% is used in accumulator batteries. Though the solder represents just a small percentage of electronic products, these devices often end on the scrap yard after their liquidation. But poisoning by lead is identified as the health menace [1].

The solders containing Pb (Pb content varies within the range from 85 up to 97wt. %) are widely employed in micro-electronic packaging industry for high temperature applications, as heavy-duty optical modules in automotive or aviation industry. The classical solder type Sn63Pb37 is (eventually was) the most used soldering alloy for soldering technology in micro-electronic industry. Its properties are considered for the reference values in the field of research of new solders. Decision in case of suitable soldering alloy is made on the basis of environmental, mechanical, physical, soldering and economic criteria. The tin based lead-free solders are mostly used solders nowadays, since tin is the most suitable alternative from among the metals with low melting point, both, from the environmental and economy viewpoint. These are mostly the combinations of tin with copper, gold and silver. But also the so-called alternative lead-free solders are used. These may be defined as the solders with high tin content and relatively low content of alloying elements, as for example: Bi, Sb, Zn, In and Ge [2].

The development of new lead-free soldering alloys continues forever due to ever expanding requirements on the substitutes for the lead containing solders. Significant attention to lead-free solders was paid recently also in the field of high-temperature applications, mainly within the soldering technologies, as for example: flip chips, ball soldering and soldering semiconductor devices [3].

In spite of numerous studies, there exists just a limited number of solders for higher application temperatures. With onset of demands for high-temperature applications the usage of high-lead solder increased rapidly. Thus, introduction of high-temperature solders and other related technologies has become an urgent priority in electronic industry. Therefore several advanced countries decided to introduce the so-called lead-free soldering with the aim to protect the life environment [4, 5, 6].

The zinc-based solders are one of possibilities of solders suitable for higher application temperatures. The Zn-based alloys are often used for fabrication of a strong joint by soldering process. However, zinc forms a thick oxide layer during soldering, which results in poor wettability and risk of cold joints. It also forms an eutectics with relatively low melting point causing loss of strength at lower temperatures. But, on the other hand it must be emphasized, that its substantial priority consists in higher application temperatures, which usually vary within the range from 300 to 420 °C. Another merit consists in its high thermal conductivity, (61 W.m-1K -1), when compared to lead solders (57 W.m-1K -1) and also tensile strength (54.7 MPa) compared to a lead soldering alloy (26.2MPa). Due these reasons it can be qualified as one of best alternatives from among the lead-free solders of present time [3].

Basic Zn solders

The zinc solders with 95% Zn and other alloying additions were developed especially for the car radiators. The solders were designed with the aim to improve the wettability, strength and corrosion resistance. Typical melting point of such solders varies around 425 °C. The solders with Zn-Al base are used especially for soldering aluminium. These provide high strength and good corrosion resistance [7].

The eutectic alloy type Zn-Al is relatively hard alloy, when compared to lead solders, but it exerts poorer wettability owing to high affinity to oxygen [5]. These alloys are used mostly for soldering aluminium alloys [8].

The alloy type Zn6Al with eutectic melting point of 381 °C is very interesting substitute of lead solders. Fig. (1) shows the phase diagram of Zn-Al, which reveals that this alloy does not form any intermetallic phases.

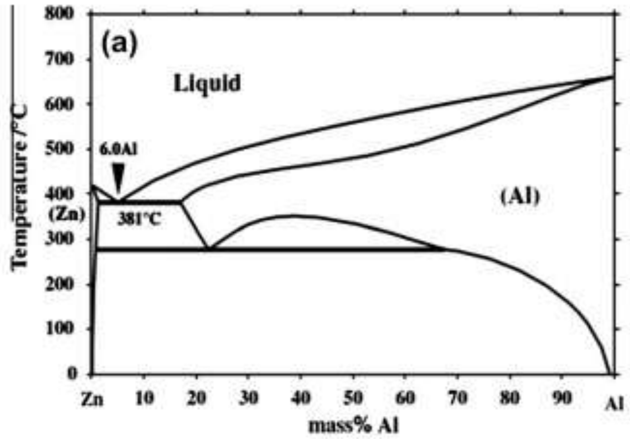

Fig. 1 Equilibrium binary diagram a)Zn-Al, b)Zn-Cu [19]

It exert fine dendritic structure, what makes it very hard and brittle. It is interesting that this alloy is brittle but at a specific composition of microstructure it becomes superplastic [9]. By adding a third element, as Cu, Mg and Ge to Zn-Al, Zn-Al-Cu and Zn-Al-Mg alloys, the formation of massive intermetallic phases is enhanced, but on the other hand it helps to reduce the melting point down to 350 °C [10]. By adding alloying elements the alloy sometimes becomes brittle with a low toughness and poor corrosion resistance [5]. Therefore it is very crucial to select the correct composition of solder for an actual application. An example of microstructure of ZnAl10Cu1,5 alloy is shown in Fig.(2).

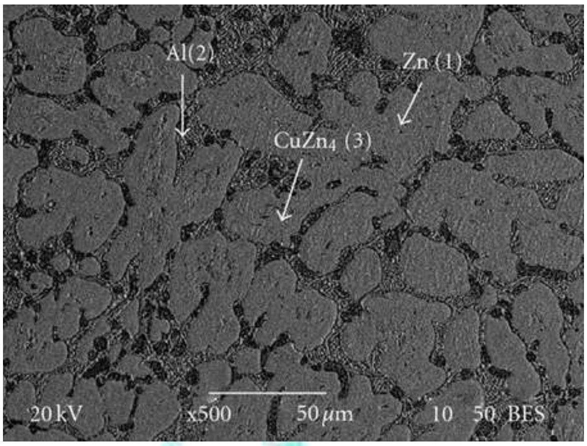

Fig.2 Microstructure of ZnAl10Cu1,5 alloy [20]

When considering the candidates from among the solders for high-temperature applications, it is supposed that the Zn-Sn alloys seem to be the most suitable solders, since these may offer good mechanical and electric properties and also economy merits. Even the slight oxidation susceptibility, should not be of much concern, since many applications of high-temperature solders are at present done in inert atmospheres. Fig. (3) shows the tensile strength as a function of Sn content measured at room temperature. The strength is gradually increasing to 22, 28, and 32 MPa with reducing Sn content; the values of joint strength are equal as in the case of SnPb37 /Cu [11].

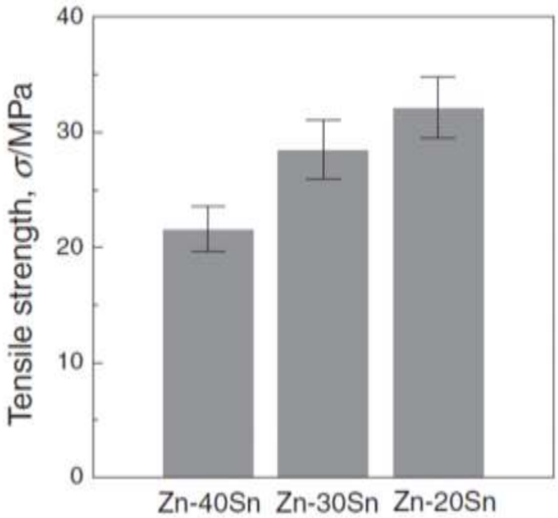

Fig.3 Tensile strenght of Zn-Sn alloy /Cu joints [23]

The researches have designed another alternative of lead-free soldering alloys, namely Zn – xSn (x = 20 wt. %, 30 wt. % and 40 wt. %). Their research has shown that Zn-Sn alloy offers suitable properties (relatively high melting point) for high-temperature applications. They also exert better toughness in comparison with other Zn – based alloys and it is comparable to Zn-Al alloys. They provide also excellent electrical properties and high resistance to oxidation at elevated temperatures [3].

Fig. (4) shows a typical microstructure of Zn-Sn solder, which is primarily composed of dark and bright phases of α -Zn and eutectic phases of Sn-Zn (α -Zn and β -Sn) [3].

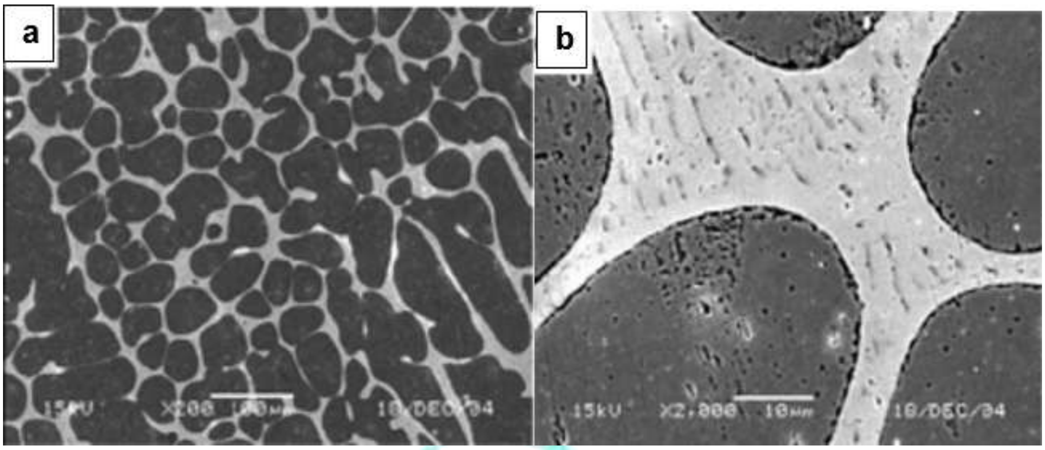

Fig. 4 Microstructure of Zn–20Sn solder; [3]

Zn30In is another potential lead-free alloy and its microstructure is primarily formed of α-Zn phases and eutectic β-In/α-Zn phases. The DSC analysis of this hypereutectic alloy has shown, that it exerts two endometrial peaks, the first at 145 °C and the second at 373 °C. The coefficient of thermal expansivity of this alloy is 31.3 .10-6 K [12].

Table 1 shows the names and designation of the most used zinc alloys (with designation ZAMAK – zinc, copper, aluminium) [24].

Table 1. Most used zinc alloys (name and designation) [24]

Name	Designation
Zamak 2	ZnAl4Cu3
Zamak 3	ZnAl4
Zamak 4	-
Zamak 5	ZnAl4Cu1
Zamak 7	ZnAl4Ni
ZA – 8 (Zamak 8)	ZnAl8Cu1
ZA – 12 (Zamak 12)	ZnAl11Cu1
ZA – 27 (Zamak 27)	ZnAl27Cu2

The effect of alloying elements on melting temperature

Regarding the fact that Zn-Al alloys exert many drawbacks, it is necessary to eliminate them. The eutectic solder type Zn-5Al has a high melting point of 382°C, and it is therefore extremely hard to perform soldering at relatively low temperature around 300°C. In this case, it is inevitable that the soldering alloys would exert the composition which maintains the strength at temperature higher than 260°C. Small addition of other elements as Mg or Ga lowers the melting point and creates a ternary alloy, which preserves the criteria desired for soldering at higher application temperatures. Mg is efficient in prevention against corrosion on the grain boundaries and lowers the melting point, however by addition of excessive amount of Mg the material becomes brittle [13].

The Zn-Al-Mg-Ge alloy exerts high strength and hardness but is relatively brittle. Thus, brittle fracture might occur at application of this solder, what may cause the failures in operation of electronic devices. Therefore, greater amount of In and Sn is added to this solder, improving thus its plasticity, what will subsequeently ensure the solder resistance against brittle fracture and also the fatigue properties will thus be enhanced [14].

The Zn12AlxIn alloy (x = 0,5; 1; 1,5) was another tested subject, while its properties as melting point, thermal expansivity, electrical resistsnce and wettability on Cu and Al substrates were investigated. It was found out that In addition will reduce the melting point of alloy and increase the specific electrical resistance. The melting point in case of addition of 1 wt. % In is in the range from 370 to 376 °C. The coefficient of thermal expansivity at addition of 0.5 wt. % In is lower than in the case of Zn-Al alloy, but at 1 wt. % In it is already higher. The wetting angle on Cu substrate is higher than on Al substrate [3].

The effect of alloying elements on mechanical properties

The Zn(4-6)Al(1-5)Cu alloy, destined for higher application temperatures was designed with the melting point within 382 and 402 °C. Increased Al content improves the spreadability and specific electric resistance, but Cu content does not affect significantly these properties. The added elements increase the hardness and tensile strength. The study has revealed good properties of Zn-Al-Cu alloys, as good solderability, low specific electric resistance and good mechanical properties [15].

Liquidus temperature increased with Cu content, but in contrary, with increased Al content it was lowered. Maximum range of melting temperatures attained 50 °C and minimum 10 °C. The composition of solders in experiment varied from 4 to 6 wt. % in case of Al and from 1 to 5 wt. % in case of Cu. Spreadability was improving with increasing Al content and Cu again did not exert any significant effect on this property.

The Al and Cu elements have contradictory effect on the specific electric resistance. More wt. % Al in alloy will reduce the specific electric resistance but Cu in contrary reduces this value. The Zn-Al-Cu alloy thus exerts the specific electric resistance within the range from 6.5 to 8.5 μΩ.cm, what is lower value than in the case of Sn37Pb alloy (14.25 μΩ.cm). The specific electric resistance of individual elements is as follows: Zn (5.9 μΩ.cm), Al (2.7 μΩ.cm) and Cu (1.7 μΩ.cm)

Regardless the Al and Cu content, the microstructure of Zn-Al-Cu alloys consists of a primary ε-phase, dendritic η-phase and the eutectic/eutectoid α-η phase [16].

The scientists studied four alternative alloys (Zn6Al, Zn6Al1Ga, Zn3Al3Mg and Zn4Al3Ga3Mg), which might to substitute the classical high-lead alloy. They studied their microstructure and mechanical properties. The requirements of electronic industry are best met by the Zn-Al-Ga alloy. However, this alloys has become brittle, caused by the solubility of Ga in Zn phase, in combination with affinity of Ga to the surface of Al and Zn phases. The embrittleness may be limited by lowering Ga content in alloy and omitting Mg [9].

Addition of Sn to Zn4Al3Mg alloy resulted in reduced tensile strength. The content of Sn added to alloy had the values of 0; 6; 8 and 13.2 wt. %. Sn addition resulted also in reduced yield point and solidus temperature [17].

The effect of alloying elements on wettability

Researchers have studied the effect of Al content on the properties of Zn-Al solder, to which they gradulaly added small amount of Ce and assessed its effect on solderability, microstructure of Zn22Al alloy, mechanical properties of joint and the structure of boundary layers. The materials as Al alloy type 1060 and pure Cu were soldered in experiments. Ce content varied within the following values: 0; 0.01; 0.03; 0.05; 0.08; 0.15; 0.25; 0.5 up to 1 wt. %. The wettability of Zn22AlxCe alloy was improved when the Ce content was within 0.01 to 0.03 wt. %. The Zn22Al0,03Ce alloy exerted the largest spreadability area from among all specimens and attained the increase by 11.6 % and 29.7 % on Al, respectively Cu substrate. The results have also shown that the alloy with 0.03 wt. % Ce had higher oxidation resistance than the alloy without Ce addition. The melting point increased with increasing Ce content in alloy [18].

Application of Zn-based alloys

The development of lead-free solders has become an issue for the researchers in electronic industry, when trying to replace the Pb containing materials. The following alloys: Au-Sn, Al-Zn, Zn-Sn, Sn-Sb and Bi-Ag are the candidates for substitution of Pb solders. Anyway, the Zn-Sn solder is recommended as the best of candidates for replacing the solders with high thermal conductivity. The Zn-based solders belong to the group of solders for higher application temperatures. These higher application temperatures vary within the range from 300 °C to 440 °C. Zinc solders with admixtures of other elements attain the melting point around 420 °C, what makes them very attractive. These are applicable not only in electronics for encasing but also for optical components and the circuit modules for gradual soldering in automotive industry. The zinc alloys are typical with high thermal conductivity and reliability in dependence on other alloying elements [21]. Soldering is performed by use of zinc alloy in the form of wire.

The alloys of zinc and aluminium are ideal for soldering the aluminium components. These find application mainly in electronic industry, for example in fabrication of solar panels, in soldering power semiconductors for the cooling units, in electronic connection between the copper stick and aluminium disc etc. The high-temperature solders are broadly used for the computer motherboards or for the packaging frames, in some applications in automotive industry and also for the flip-chip technologies (S.A. Musa et al. 2013).

Applicability of Zn-ln-Mg – based solders in industry consists in perspective substitution of lead solders for higher application temperatures. These may be employed in electronic, electro-technical and also automotive industry. They are applicable also for gradual soldering in progressive technologies of encasing, as for example in the following technologies: Ball Grid Array (BGA), Flip-Chip technology (C4), Chip-Scale-Package (CSP) and/or Multi-Chip Module (MCM).

Flip-chip

Is a method for connecting semiconductor parts on the outer periphery by soldering balls (pellets), which are laid on the support chip. The solder pellets are put on the chip support, on the upper side of flap in the course of final step of processing.

The flip chips have recently gained popularity among the manufacturers of phones and small electronics, where the size savings are demanded.

The S-bond company produces many products of electro-technical character, where just the solders with high thermal conductivity are desirable, as the case of Zn based solders. We actually speak about application of solder type Zn-Al-Ag in a flip-chip module (Fig. 5) with the melting point of 400-420°C [22].

Fig. 5 Flip-chip module (S-BOND Technologies)

Zinag is an alloy composed of three metals – zinc, aluminium and silver. It is typical with excellent mechanical and anti-corrosion properties and low weight. It is applicable mainly in aviation and space industry, medicine and in automotive and construction industry [24].

Sensors

There exist many types of sensors for different types of measurement as for example the sensors for measuring: stress, strain, temperature, pressure etc. Great number of sensors must be enclosed due to their protection. It is possible to join a number of different metals, ceramics and glass which are usually used in enclosed spaces or packages. In this case the solder type Zn14Al may be used for soldering, offering thus the strength of soldered joints of 80MPa [23]. Fig. (6) - A, B shows several types of sensors manufactured by use of Zn – based solders [22].

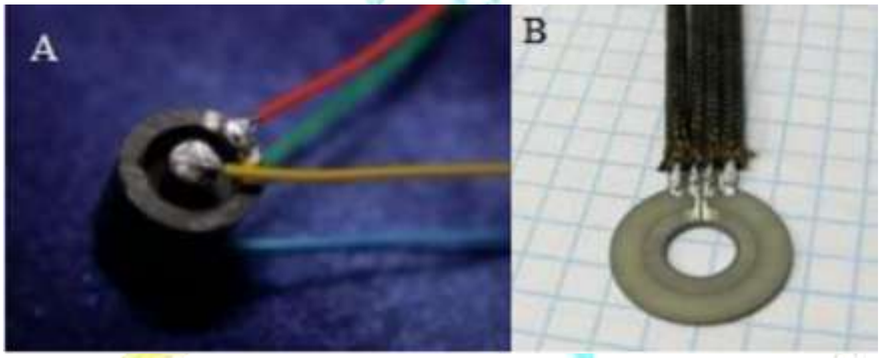

Fig. 6 Sensors (S-BOND Technologies)

Superloy alloy (containing 6.6 – 7.2 % Al and 3.0 – 3.6 % Cu) offers excellent creep resistance. It is used for die casting on the machines with hot chamber, ensuring a high accuracy of castings. Superloy is thus a materials suitable for applications where a compromise between precise dimensions and high mechanical propeties is necessary. It is extremely suitable for electrotechnical parts, connectors, adapters and small precise parts [24].

Automotive industry

The Zn – based solders are used also in the automotive and transport industry, actually in temperature control, in battery connections and in electric transfer of energy. Together with the commercial onset of hybrid and electric cars also the applications as heavy-duty cooling, electronic appliances and connecting the battery terminals have occurred. All the mentioned necessitates also new procedures and technologies. The Zn – based soldering alloy is used for soldering the aluminium/copper combination without flux and offers strong joints without voids and pores. Such joints are typical for cooling the boards, used in the cooling panels for solid electric components in hybrid and electric vehicles. There are at present several racing cars in Formula 1, which have attained their excellent position thanks to S-bond solders [22].

These powerful cars shelter the braking power, save the fuel to acceleration in order to achieve the desired speed. That all is controlled by the so-called KERS. The core of KERS consists of power transducer and semiconductor electronics, which require an efficient operation of thermal device. The transducer of core power is powered by semiconductor tranzistors, which generate huge amount of heat that must be dissipated to aluminium distributor and thereof to the air via a fin radiator [22].

The zinc solders with 95% Zn and other additives were developed especially for the car radiators. These find application also in the repairs of joints of air conditioning coils. Zn-Al alloys were for a long time applied as high-temperature alloys for structural applications. From the viewpoint of soldering in electronics at high application temperatures, these alloys seem to be very perspective, mainly owing to lower price compared to Pb.

II. Conclusion

The aim of research was to summarize the knowledge about the need of lead-free solders applicable for higher application temperatures. The mentioned findings suggest that from the environmental viewpoint any further application of lead – based solders is inadmissible. That´s why these were substituted by the lead-free solders. One of possible substitution of lead in solder have brought the Zn – based solders, which most approach the Pb solders by their properties. The biggest advantage of Zn – based solders consists in their high melting point, and therefore they can be applied in the joining process utilizing high temperatures. By addition of certain elements, the properties of this solder can be adapted, as for example high electrical resistance by addition of In; high spreading rate by increasing Al proportion; higher hardness (Mg); reduced oxidation (Zn-Al-Mg), improved wettability (Zn22AlxCe) etc. Thanks those priorities, these types of solders are finding application mainly in the electronic and chemical industry and may be used also in the repairs of some aluminium parts. Soldering with Zn – based alloys remains the subject of future research.

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