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Hardness of the solder alloy Cu-In-Sb in dependence of the molar ratio of the components

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Abstract: An increasing concern for environmental protection led to the establishment of strict provisions regarding the use of alloys that could have a detrimental effect on the environment, which resulted in reduction of use lead solder materials. Copper-based alloys in particular represent a possible replacement for standard not-lead solder. Alloys on the basis of copper, indium, and antimony are important in production of new solder materials. Thus, it is desirable the knowledge about different ratios of mentioned elements in these alloys, related to their influence on the mechanical properties of alloy, for the development of new high quality solder materials. In this paper, the hardness of ternary system Cu-In-Sb was investigated, for three vertical cross sections with molar ratio: Sb:Cu = 1, Cu:In = 1, Sb:In = 1. Highest hardness has been found with 0,30 mol fraction of copper in Cu-InSb vertical cross section. Hardness continually decreases with the increas of molar percent of antimony. Indium has shown the least variation and influence on the hardness of these alloys. The most variation in hardness was during the change of the molar fraction of copper, which indicates that the copper is the most important element for the hardness of this system.

INTRODUCTION

The industry uses large amounts of alloys based on lead due to its physical and chemical properties and low cost. Lead toxicity poses a major threat to the environment, and scientific research has begun to accelerate the industrial development of new ecological materials to completely eliminate the use of existing alloys based on lead (Smith, 2004). New solder materials, environmentally more acceptable, should not contain lead and that's mentioned in the European Union directives (EU Directive 2008/34/EZ). The development of unleaded alloys is one of the world's environmental trends. Alloys on the basis of copper, indium and antimony are important in production of new solder materials - possible replacement for traditional lead solder.

Indium is a silver soft metal with relatively low melting point. Same as sodium, indium can be cut with an ordinary knife. For a human organism, indium is not an essential element but also very little is known of its toxic properties (Oberndorff, 2001; Liu *et al.,* 2003). Elemental indium could has a significant effect on changes in the microstructure of the alloy, from the aspect of the formation of intermetallic compounds with copper (Liu *et al.,* 2002; Manasijević *et. al.,* 2009). Indium is primarily used as a soldering material. Antimony is glossy gray metal with low-hardness. Four allotropic modifications of this element are known. Antimony is easily alloyed with a large number of metals, improving their mechanical properties. Its characteristic is that it is corrosion resistant and easily merged with other metals (Liu *et al.*, 2003). Antimony is considered strategic raw material (Gomidželović *et al.,* 2009). The effects of antimony and its compounds on human health and environment differ widely (Oberndorff, 2001). Surely, some antimony compounds are toxic. The copper is relatively soft metal, it can be shaped well. As an excellent conductor of heat and electric current he found many applications in the technique. Copper is very often part of many alloys, probably it is the most used metal in technology of alloys. Elemental copper in its basic state is not poisonous, but copper ions are very strong poisons for microorganism. Copper alloys are important technical materials with excellent mechanical properties. They are extremely resistant to corrosion and wear. In this sense, copper based alloys have good characteristics that are desirable for their application in the electro and mechanical engineering (Oberndorff, 2001; Smith, 2004; Liu *et al.*,2000).

Cu-In and Cu-Sb alloys are well known binary system in engineering of alloys, and already have a usage in electro and mechanical industry (Liu *et al.,* 2002; Gierlotka and Jendrzejczyk-Handzlik, 2009; Liu *et al.,* 2000). These two systems, especially relation between Cu and In, are the reasons for the research of this Cu-In-Sb alloy. Indium and copper react and form intermetallic compound that is much harder and stiffer than the parent indium and copper. As well, this binary system, as contact material, is thermally very stable, and that is important in electro industy (Liu *et al.,* 2002). Ternary system Cu-In-Sb belongs to a group of new unleaded solder materials. Regardless of significant application there is insufficient data in the literature on the mechanical properties of this system. All this provides sufficient space for research in this field, in terms of contribution of knowledge about the mentioned ternary system, which besides the theoretical contribution and importance, should enable the technical application of this research. The system Cu-In-Sb, exactly its hardness, is the main goal of the research, so far not examined, which provides the possibility of research in this field.

Hardness presents one of the mechanical properties of the material. Hardness of material implies the resistance that the material show when a harder body penetrates through its surface. It is expressed by the ratio of force per unit of the surface of the imprint, or by the depth of the imprint in the material, expressed in the corresponding hardness units. In this study, the hardness of Cu-In-Sb alloy was determined, according to the Brinell method.

EXPERIMENTAL

Hardness of material is the property of the material which enables it to resist plastic deformation, usually by penetration or by indentation. The Brinell hardness test procedure is governed by several standards depending on the type of material. This hardness testing procedure was suggested by the Swedish engineer Johan August Brinell in 1900, and it was the first widely accepted and standardized method of hardness testing in material science. Brinell method of measuring the hardness consists of hardened steel or tungsten-carbide ball against the smooth material surface under standard test condition. Standard test condition resumes diameter of ball, load (force, pressure) and period. The dept of ball penetration depends on the type of material being tested.

Sample preparation

The preparation of the samples was carried out with 99.99% purity metals (Alfa Aesar GmbH, Germany). The corresponding masses of copper, antimony and indium were weighed, crushed and mixed. The stirred samples were melted in a quartz furnace under vacuum (Becej, KP 03-30). Samples were gradually heated to a melting point and maintained at the same temperature for a further 30 min. The quartz tube with the dissolved sample was cooled to room temperature. The weight of the prepared alloys was 3g. The loss of antimony due to evaporation was up to 3%, so the antimony was added to excess of 3%, as compensation for weight loss during sample preparation.

The samples were brushed with abrasive papers made of SiC, Al_2O_3, Al_2O_3 + Fe_2O_3 and grain size 3 according to ASTM. After brushing, they were polished on several rotary discs that are coated with the felt. The speed of rotation of the disc can be changed, if necessary, but not exceed 15000 rpm. Fine polishing was done manually with alumina Al_2O_3 suspension.

After completion of the polishing, the samples were washed with distilled water and alcohol and dried in a stream of warm air. The samples, thus prepared, are free from any visible irregularities and impurities in order to obtain more accurate results of hardness measurement (ASTM, 2011; Marković, 2013; Kraut, 2009).

Conditions of test

The surface of the sample must be clean and polished. The thickness of the sample must be at least 8-10 times higher than the depth of imprint. No traces of deformation must be seen on the back of the sample after measurement. The distance between the center of the print and the edge of the sample should be cared, as well as the distance between the two adjacent prints during multiple measurements. The angle between the axis of the impeller and the surface of the sample must be 90°, which is achieved by surface treatment and the adjustment of the stand (SRPS JUS C.A4.030). The entire process of alloys testing was carried out at room temperature.

Test procedure

The ball for imprinting (impeller) was placed in the carrier, the surface of the sample is lighted, prepared sample was placed on the stand and tightened with the impeller carrier. With the activation of device the injection was performed. After imprinting, the sample was released and the diameter of the print was measured. Diameter reading was performed using a microscope (1/100 mm accuracy). The accuracy must not be less than 0.25% of the diameter of the ball (SRPS JUS C.A4.030). The used force was 25.2 N for a period of 15 s and ball was made from hardened steel. The process testing was carried out at 23 °C.

The hardness, by the Brinel method (HB), is defined as the ratio of the force of the imprint and the surface of the print, formed by the ball that was imprinted in the surface of the test material. Brinell hardness is calculated: HB = F / A . A is the surface of the imprint (mm2). F is the injection force (N).

Apparatus
Hardness measurement was done on the Brinell apparatus of the manufacturer Plasmait GmbH (Lebring, Austria). Results were expressed as mean value ± standard deviation (SD) of triple measurements. Unit is Brinell's hardness number HB that is in correlation to MN/m^2 (MPa).

RESULTS AND DISCUSSION

Various combination of molar fraction of ternary alloys (Cu-In-Sb system), from three vertical sections (Cu-InSb, In-CuSb and Sb-CuIn), were experimentally investigated on the hardness by Brinell method. All results of the measured hardness are given in the Table 1. The results are expressed as mean value of the triple measurements ± standard deviation (SD). Function of hardness from molar fractions of the elements (quasi-binary cross sections) are graphically presented in Figures 1, 2 and 3.

Table 1. Brinell hardness (HB) of the alloys from the Cu-InSb , Sb-CuIn and In-CuSb vertical sections

molar fraction x_i (Cu,Sb,In)	HB Cu-InSb ± SD (MPa)	HB Sb-CuIn ± SD (MPa)	HB In-CuSb ± SD (MPa)
0.0	280.0 ± 10.0	243.0 ± 25.0	150.0 ± 18.0
0.2	303.3 ± 5.8	223.7 ± 36.6	135.0 ± 18.0
0.4	305.0 ± 15.0	220.0 ± 26.6	126.0 ± 23.3
0.5	295.0 ± 10.0	218.0 ± 35.4	143.3 ± 5.8
0.6	276.7 ± 12.6	215.0 ± 6.0	166.7 ± 12.6
0.8	275.0 ± 17.3	204.7 ± 16.7	138.0 ± 23.1
1.0	290.0 ± 0.0	220.0 ± 0.0	145.0 ± 0.0

Dependence of hardness in function of the molar fraction of the antimony (Sb-CuIn vertical section) is shown in Figure 1. There is decreasing of hardness with the increasing of Sb content to 80 %, and after 80 % there was enhancement of hardness. Main reason for decreasing of hardness on the Figure 1. is tight binary system of indium and copper, and addition of antimony disturbs this strong intermetallic connection and leads to reduction of hardness (Liu *et al.,* 2002). On the base of results, in order to increase hardness, it is assumed that antimony is used in smaller concentrations. This assumption certainly increases the ecological acceptability of the alloy regarding that some antimony compounds are toxic. The content of the antimony in the alloys usually ranges from 1 % to 20%, in solder alloys its usually about 5% (Ipser *et al.,* 2007).

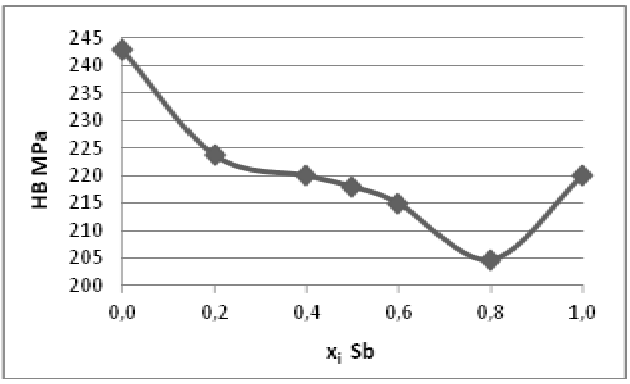

Figure 1. *Brinell hardness of alloys in the Sb-CuIn vertical section*

The hardness of alloy vary with the contents of the copper (Cu-SbIn vertical section). The highest hardness was recorded for copper molar content of about 30 % in the Cu-SbIn vertical section. Alloys with copper content greater of 30 % have a declining hardness. Minimum of hardness was found for alloy with of 80 % of copper in the vertical sections Cu-SbIn (Figure 2). Copper is the most used element in alloying. Its content improves the mechanical properties of many technically important alloys, even in the small presence (Oberndorff, 2001). In this research copper proved to be the most influential element for the hardness of tested Cu-Sb-In ternary system.

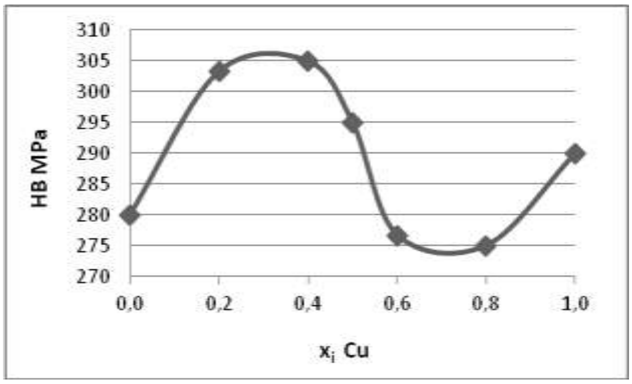

Figure 2. *Brinell hardness of alloys in the Cu-SbIn vertical section*

The dependence of the hardness in function of the indium molar fraction, from In-CuSb vertical section, is given in Figure 3. Minimum of hardness was found for 40 % of indium molar fraction. From 40 to 60 % of indium content, hardness grows rapidly in the In-CuSb vertical section. The content of indium is the most significant from the aspect of the price of the alloy because its price on the market is still high, but with the tendency of significant fall in recent years (Kellya and Matos, 2014). On the other hand, more presence of indium generally reduces the melting point of the alloy and that is important for the solder material (Ipser *et al.*, 2007, Oberndorff, 2001). Regard of hardness, according to the vertical In-CuSb section, the most preferred amounts of indium are in the range of 40 - 60 %.

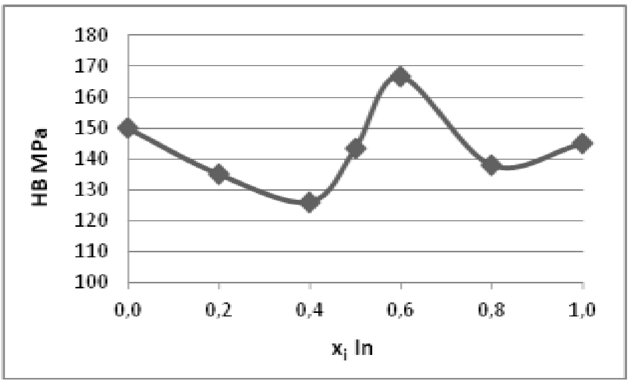

Figure 3. *Brinell hardness of alloys in the In-CuSb vertical section*

The content of the elements for the purpose of high hardness of the alloy should be at intervals of significant increase of hardness in the vertical sections for individual elements. High hardness of tested ternary system should be expected in alloys with low antimony content, indium in content of about 50 % of molar ratio and copper round 30%.

Melting point and electrical conductivity are significant properties of materials that used for soldering. The melting points of the various molar combinations of this ternary system range from 430 °C to 510 °C (Manasijević, 2009). In general, with the increase of the indium molar fraction, the melting point of the alloy decreases. Increasing the copper and antimony molar ratio generally increases the melting point of the alloy (Manasijević, 2009). The electrical conductivity of various molar combinations of this triple system ranges from 0,9 MS/m to 10 MS/m, which certainly meets the requirements of the solder material (Aljilji, 2010).

This ternary system has shown very good thermal stability, practically the same on the 25 °C and 400 °C, and that is also very important for solder material (Aljilji, 2010).

Finally, the presented results for new solder materials based on indium, antimony and copper are significant improvement compared with lead based alloys. The most important aspects of improvement are mechanical property (hardness), thermal stability and ecological properties.

CONCLUSIONS

The low content of the antimony, in the tested Cu-In-Sb ternary system, is recommended for purpose of higher hardness, potentially less toxicity and environmental protection aspects. Copper is the most influential on the hardness of this system. The higher content of the indium lowers the melting point of the alloy, which is important for the solder material, but the greater content of the indium increases the price of alloy. The melting point is higher than many others solder materials, but on the other hand there is a very good thermal stability, and the hardness significantly exceeds most of the solder materials, so the possibility of cracking and physical damage to the soldering weld are lower. High hardness of the solder material can be very significant in some specific production needs.

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Summary/Sažetak

Povećan interes za zaštitu životne sredine rezultirao je smanjenjem ili potpunim odstranjenjem iz upotrebe olovnih lemnih materijala. Legure na bazi bakra predstavljaju potencijalnu zamjenu za ovu vrstu olovnih legura. Legure koje, pored bakra, sadrže indijum i antimon pokazale su se kao dobar materijal za lemljenje, nove generacije. Svakako, poželjno je poznavati uticaj količinskih omjera pojedinih elemeneta (Cu, In i Sb) na fizička svojstva ove legure. Ovim radom ispitivana je tvrdoća trojnog sistema Cu-In-Sb u ovisnosti od molarnog udjela komponenti. Najveća tvrdoća nađena je u 0.3 molarnoj frakciji bakra u vertikalnom presjeku Cu-InSb. Zaključeno je da tvrdoća opada sa porastom molarnog udjela antimona. Promjene molarnog udjela indijuma su pokazale najmanje varijacije i uticaj na tvrdoću ove legure. Najviše promjene u tvrdoći bilo je kod promjena molarnog udjela bakra pa se on pokazao kao najvažniji element za tvrdoću ovog trojnog sistema.