U.P.B. Sci. Bull., Series B, Vol. 86, Iss. 1, 2024. ISSN 1454-2331

RESEARCH ON THE DEVELOPMENT AND CHARACTERIZATION OF Bi-Sn, Bi-Sn-Sb AND Bi-Sn-Ag SOLDER ALLOYS

Gheorghe IACOB[1], Valeriu-Gabriel GHICA[2], Mircea-Ionuţ PETRESCU[3], Florentina NICULESCU[4, *], Mihai BUŢU[5], Constantin-Domenic STĂNCEL[6], Mariana-Mirela STĂNESCU[7], Andrei-Alexandru ILIE[8]

Different types of lead-free solder alloys were obtained by processing them in an electric induction furnace and gravity casting. The effects of adding Sn, Ag and Sb on the microstructure, melting behavior and mechanical properties of the obtained alloys were investigated. Optical microscopy analysis emphasizes the formation of a homogeneous and well-defined structure of the Bi-Sn-Sb alloys, and a lamellar-globular structure is observed, with compounds spread throughout the mass of the material for the Bi-Sn-Ag alloy. For chemical analyses were used different spectrometric methods. The hardness of samples was determined by Leeb method.

Keywords: solder alloys; Bi-Sn; antimony; silver; characterization.

1. Introduction

Soldering is a process in which two or more metals are joined together by melting and flowing a filler metal (solder) into the joints with a melting temperature well below that of the substrates and usually less than 450°C. The term "solder" refers to a group of metal alloys that melt at relatively low temperatures and whose purpose is to form a joint between two other, possibly dissimilar materials [1].

The increase in demand for electrical and electronic devices in which printed circuit boards are incorporated makes solder alloys more and more in demand on the market. This increase is mainly associated with the electronic field and the automobile industry, a large consumer of such alloys. Another influencing factor is represented by the rise in demand for the semiconductor industry. Research in this field is always up to date, being carried out to obtain new types of soldering

[1] Assoc. Prof, Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: iacob_gh@yahoo.com
[2, 3, 5, 6, 7, 8] Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania
[4, *] Lecturer, Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, *corresponding author, e-mail: flori.pereteanu@yahoo.com,
[7] Lect., Faculty of Applied Sciences, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: mirela.stanescu@physics.pub.ro

alloys from various systems that meet the increasingly stringent requirements of manufacturers and especially end consumers [2 - 9].

On the profile market, the most representative and most used alloy system is Sn-Pb, in which the proportions between the two elements revolve around the concentration of 63Sn with 37Pb (in weight percentages) which represents the eutectic point of the alloy system at a temperature of 183°C, offering better wetting behavior and mechanical properties [9 - 12].

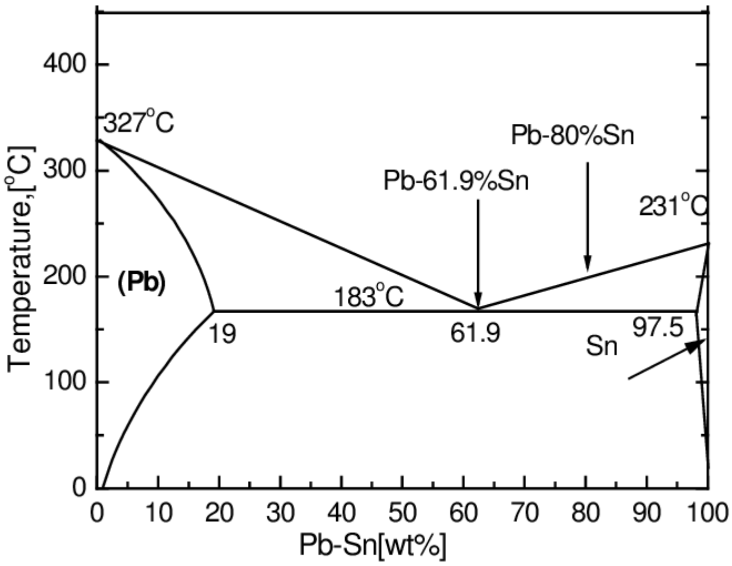


Fig.1. Binary eutectic phase diagram for the lead-tin alloy system [11]

Observing over time that the toxicity of Pb leads to great health problems thar appear with the accumulation of small quantities in human body (affect physical, neurological functions), through environmental regulations (European Union through the Restriction of Hazardous Waste – RoHS and Waste Electrical and Electronic Equipment directives, Turkey, Japan, China, South Korea, California – USA and other countries and states are still debating) it was established that it is necessary to replace it and possibly the complete removal from the component of solder alloys with lead content and conducting intensive research to find feasible options that can replace it in the medium and long term [13 - 15].

Nowadays there is a high demand in the market for solder alloys without lead and other toxic elements to be used in electrotechnical, electronic and other industrial fields. However, the development of new lead-free solders requires adequate thermophysical properties because the drawbacks of newly developed alloys are the formation of large intermetallic compound, low wettability and thermal shock resistance. Now, many variants are being researched, most of them having Sn as the basic element being alloyed with elements such as Au, Ag, Bi, In, Zn, Sb and Ge [2, 3, 5, 6, 8, 9, 16 - 19].

Bismuth is used to lower the melting point of solder alloys; it is mainly used in fusible alloys. Due to its high oxidation rate, it will inhibit wetting. Tin provides the best wettability of soft solder alloys; it is an aggressive element that dissolves most of the metals it meets during soldering. Tin is also soluble in most other low-melting metals and forms alfa and beta metal phases. In the alpha phase, the other metal is dissolved in the tin, and in the beta phase, the tin is dissolved in the other metal. Silver is used to reduce silver removal from thick silver film circuits. It slightly inhibits wetting and improves the mechanical strength of alloys. Stibium (antimony) is normally used as a hardening agent. Due to its high oxidation rate, it inhibits wetting by changing the surface tensions of the solder [1, 2, 5, 6, 8, 14].

One suitable candidate for replacement of classical alloys is Sn-Bi alloy system but are still several problems to be solved. Due to the low-temperature eutectic (138°C) it cannot be used in most of the electronic applications. Poor wettability and the brittleness of these alloys are other disadvantages that requires improvements, and this can be resolved mainly by incorporating additional alloying elements or increasing the content of Bi [20].

Ecological, polluting and economic considerations together with care for the environment make the field of soldering alloys to remain an area of major interest if there is still a high demand for such products. Due to the decrease in the melting temperature, the use of these types of alloys has a minor economic impact, an important variable that can influence the final price of various electronic components. This characteristic provides a competitive advantage in terms of quality/price ratio for the alloys produced.

2. Materials, methods and experimental

The research carried out in the Hydrometallurgy Laboratory within the Department of Engineering and Management of Obtaining Metallic Materials of the Faculty of Materials focused on the development of easily fusible metal alloys Bi-Sn, Bi-Sn-Ag and Bi-Sn-Sb (Fig. 2), with new chemical compositions, the microstructural characterization and the determination of its hardness to establish some starting points for future research.

Bi (purity 98.9%), Sn (purity 99.6%), Ag (purity 97.5%) and Sb (purity 99.9%) were used to develop the solder alloys. Crucibles based on graphite and magnesite were used for melting and casting easily fusible metal alloys of the Bi-Sn class (with addition of Ag and Sb). As protection and refining flux: NH_4Cl and KCl (ratio 1:4). The primary preparation was aimed at checking the quality of the raw materials and auxiliary materials and bringing them to optimal sizes and weights for use in the alloy production process. The metals and the coating (protection) and refining flux were dosed by weighing on an electronic balance.

Fig.2. The raw materials used for elaboration, the presentation of the induction furnace and the resulting samples after melting: 1 - Bi60Sn40; 2 - Bi60Sn35Sb5; 3 - Bi60Sn35Ag5

The melting and casting process took place in three stages, in the normal working atmosphere, as follows:

I. In the first stage, the Bi-Sn alloy was developed as follows: the furnace temperature was set to 300^0C, the furnace due to the tolerance of ± 20^0C reached the temperature of 320^0C after approx. 15 minutes, and then we waited about 5 minutes for the temperature to drop to the set temperature and the measured amount of Bismuth and Tin was introduced into the crucible.

II. In the second stage, the Bi-Sn-Sb alloy was developed as follows: the furnace temperature was set to 650^0C, the furnace due to the tolerance of ± 20^0C reached the temperature of 670^0C after a time of approx. 30 minutes, and then we waited about 10 minutes for the temperature to drop to the set temperature and the measured amount of Stibium was introduced into the crucible.

III. In the third stage, the Bi-Sn-Ag alloy was developed as follows: the furnace temperature was set to 980^0C, the furnace due to the tolerance of ± 20^0C reached the temperature of 1000^0C after a time of approx. 25 minutes, and then we waited about 15 minutes for the temperature to drop to the set temperature and the measured amount of Silver was introduced into the crucible. After melting Ag, the other elements - Bi and Sn - were introduced.

Magnesite crucibles were used for melting and casting easily fusible metal alloys of the Bi-Sn class (with addition of Ag and Sb), which show both high refractoriness and high resistance to chemical attack of the alloy. It is considered necessary to obtain in the laboratory phase some types of such alloys to study their properties, so that a certain type of alloy can be chosen that ensures optimal processing and casting properties.

Considering that the new alloy compositions have not been studied, detailed chemical analyzes were carried out, to obtain the most realistic values of the content in the basic elements, as well as for other elements that can be included as impurities, brought by primary metals.

Each analysis method has advantages and disadvantages in terms of measurement tolerances, or minimum limits for element identification. For the alloys used for soldering, to establish the subsequent phenomena regarding adhesion, wettability, electrical conductivity, etc., it is necessary to know in detail the chemical composition and especially if there are elements that can interfere or worsen these phenomena. The chemical characterization was performed using a:

- Beckman SpectraSpan System V emission spectrometer that combines a high-resolution direct current energy and plasma ICP with the excitation source, high-resolution Echelle a high-performance instrument.

- Thermo Scientific Niton XL2 analyzer that offers high performance and advanced electronics while maintaining the point-and-shoot simplicity that is the hallmark of all X-ray fluorescence (XRF) instruments. Provides immediate non-destructive chemical analysis of investigated alloys.

- Z-200 portable metal and alloy analyzer that is the most capable ever created by LIBS SciAps. Its advanced technology includes an integrated argon purge to provide more accurate results. Laser surface cleaning virtually eliminates surface preparation. Laser scanning of impact points greatly increases the accuracy of the analysis. The Z-200 portable analyzer is perfectly suited for in-situ analysis of metals and alloys.

The microstructural analysis was performed with the Optika B383 MET optical microscope, equipped with a digital camera and image processing software.

The determination of hardness was carried out using the Portable Digital Durometer, manufactured by SAUTER – Germany, model HMM, by the impact method, using a recoil probe, in any of the usual units (directly or by conversion according to DIN 50150 or ASTM E140): HV, HB, HRB, HRC, HL, HSD and N/mm^2.

3. Results and discussion

The samples from the obtained Bi-Sn, Bi-Sn-Sb and Bi-Sn-Ag alloys were characterized by optical microscopy analysis, chemical composition determination and hardness determination. To obtain the most conclusive results regarding the chemical composition of the alloys resulting from the elaboration processes, three different types of chemical analysis were carried out and presented as follows:

The chemical characterization performed with the plasma optical emission spectrometer - DCP, is shown in Table 1.

Table 1

The results of the chemical analysis by plasma optical spectrometry

Sample alloy	Bi	Sn	Sb	Ag	Others	Total
Sample 1 Bi60Sn40	60.1	39.49	-	-	0.41	100
Sample 2 Bi60Sn35Sb5	60.4	34.1	4.87	-	0.63	100
Sample 3 Bi60Sn35Ag5	60.6	33.9	-	4.95	0.55	100
Values are expressed in %						

The chemical characterization performed with the portable X-ray spectrometer is shown in Table 2.

Table 2

The results of the chemical analysis by X-ray spectrometry

Sample alloy	Bi	Sn	Sb	Ag	Zr	Zn	Cu	Others	Total
Sample 1 Bi60Sn40	59.12	40.62	-	-	0.191	-	-	0.07	100
Sample 2 Bi60Sn35Sb5	58.28	36.23	5.36	-	0.126			0.004	100
Sample 3 Bi60Sn35Ag5	58.96	37.91	-	2.83	0.163	0.054	0.080	0.003	100
Values are expressed in %									

The chemical characterization performed with the portable laser spectrometer is shown in Table 3.

Table 3

The results of the chemical analysis by laser spectrometry

Sample alloy	Bi	Sn	Sb	Ag	Cu	Pb	Fe	Al	Si	C	Total
Sample 1 Bi60Sn40	59.529	39.348	<0.0278	-	0.058	0.028	0.023	<0.000291	<0.975	0.011	100
Sample 2 Bi60Sn35Sb5	59.378	34.486	5.07	-	0.210	0.129	0.034	<0.000404	<0.689	<0.00356	100
Sample 3 Bi60Sn35Ag5	58.91	34.332	0.0242	4.74	1.49	0.099	0.034	<0.00183	<0.337	<0.032	100
Values are expressed in %											

Due to the compliant chemical composition, we will expect the casting structure to also comply with the composition of the constituents indicated in the equilibrium diagram corresponding to the Bi-Sn base alloy. Some variations in the concentrations of Bi and Sn are observed in the analyzed samples, and the differences can be included in the detection limits of the devices used or in the measurement tolerances, as well as the appearance of small concentrations of other elements that were detected, most likely coming from the chemical composition of the materials used in the elaboration Bi (purity 98.9%), Sn (purity 99.6%), Ag (purity 97.5%) and Sb (purity 99.9%).

The hardness of Bi-Sn, Bi-Sn-Sb and Bi-Sn-Ag alloy samples was determined by the impact method (or based on the rebound force of the tungsten carbide ball inside), starting from the left of the sample to its right, calculating the average of these values. Table 4 presents the results after determining the hardness by the Leeb method and the average values of the alloy samples that were studied in this work.

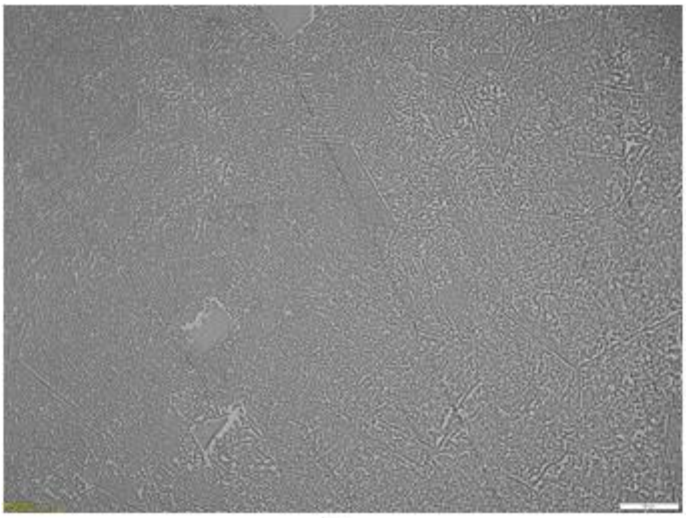
Table 4

The results of tests to determine the hardness of alloys

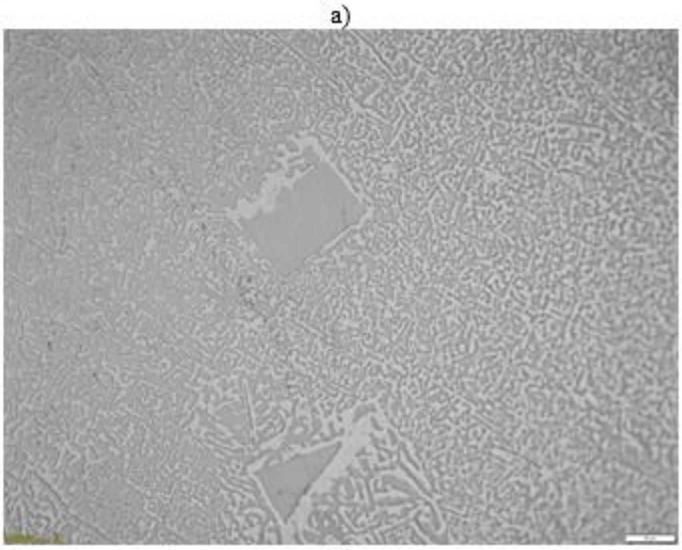
Alloys	*Leeb Hardness, HL*	*Average*
Sample 1 - Bi60Sn40	233, 78, 90, 65, 61, 89, 197, 255, 76, 169, 164, 114, 81	**128.6**
Sample 2 - Bi60Sn35Sb5	229, 119, 87, 90, 91, 76, 174, 167, 124, 289, 131, 106, 74	**135.2**
Sample 3 - Bi60Sn35Ag5	281, 167, 91, 120, 216, 162, 80, 229, 94, 63, 176, 58, 89	**140.5**

The increase in the hardness of sample 3 compared to sample 1 is observed. The values taken are between 61 - 255 HL for S1 (average - 128.6), 74 - 289 HL for S2 (average - 135.2) and 58 - 281 HL for S3 (average – 140.5).

The optical microscopy characterization of the alloy samples was carried out. Before studying under the microscope, the samples were ground and polished to highlight the structure of the obtained material. Several images were taken from the analyzed sample at different eyepiece sizes to obtain a more conclusive microstructural analysis. In the images below we can see that the surface of the cast alloys is homogeneous, free of pores or other casting defects, meaning that the process was conducted properly. At the same time, the beneficial influence of the refining flow led to this result. The images from Fig. 6 show the microstructures of the Bi60Sn40 alloy, at different magnifications of the objective.



a)



b)

Fig.6. Optical microstructures of the Bi60Sn40 alloy sample: a) magnification x200, scale 20 μm and b) magnification x500, scale 50 μm

According to the microstructural analyzes of the cast alloys, the much more homogeneous and well-defined structure, even almost eutectic, of the Bi60Sn40 and Bi60Sn35Sb5 alloys is highlighted. The microstructure of Bi60-Sn40 solder alloy highlights a structure composed of the brittle Bi phase and the ductile β-Sn phase. The Bi-Sn system is a simple binary eutectic, with Bi having moderate solubility and not forming intermetallic compounds with Sn. According to the data in Table 3, in this sample there is a concentration of 0.058% Cu, which can lead to the formation of Cu_6Sn_5 compounds in the structure. The images from Fig. 7 show the microstructures of the Bi60Sn35Sb5 alloy, at different magnifications of the objective.

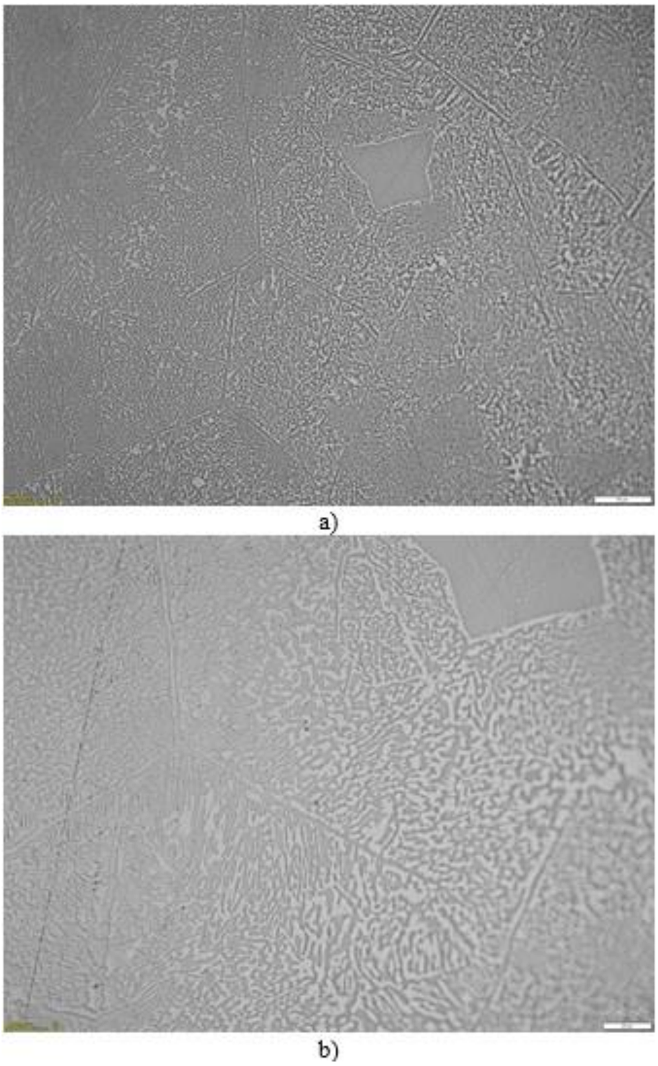
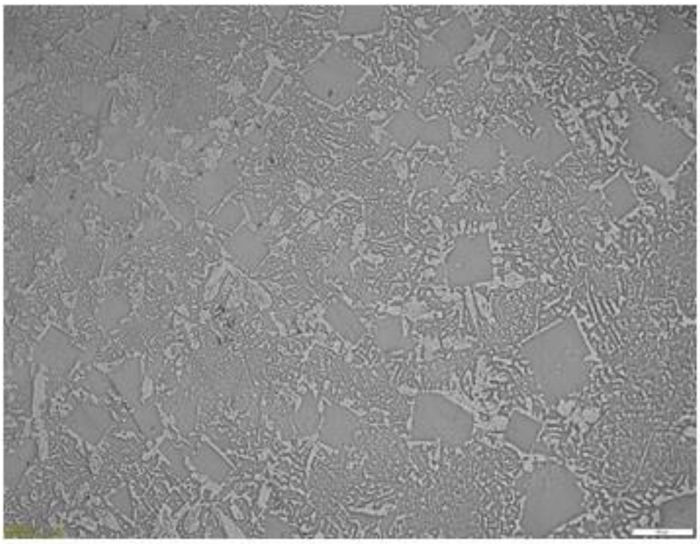
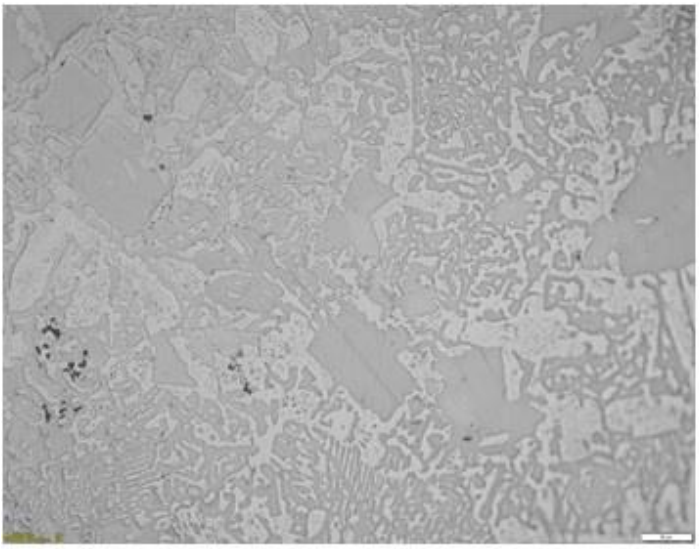


Fig.7. Optical microstructures of the Bi60Sn35Sb5 alloy sample: a) magnification x200, scale 20 μm and b) magnification x500, scale 50 μm

Addition of Sb to Bi-Sn alloy led to a refining of the grain size and produces SnSb intermetallic compound (like needles). SnSb is dispersed in the Sn phase near the grain boundaries of the eutectic structure and suppresses the growth of the eutectic structure. Besides this, the formation of Cu_6Sn_5 compounds is also observed, due to the content of 0.21% Cu in the analyzed sample (Table 3).The images from Fig. 8 show the microstructures of the Bi60Sn35Ag5 alloy, at different magnifications of the objective.



a)



b)

Fig.8. Optical microstructures of the Bi60Sn35Ag5 alloy sample: a) magnification x200, scale 20 µm and b) magnification x500, scale 50 µm

Compounds appear in both samples, but their degree is significantly lower than for the Bi60Sn35Ag5 alloy, where the formation of a lamellar-globular structure is observed, with many compounds primary large Ag_3Sn and Cu_6Sn_5, spread throughout the mass of the material, due to the high percentage of Ag (4.74%) and Cu (1.49%) in the composition of the alloy (Tables 1 and 3).

4. Conclusions

The alloys Bi60Sn40, Bi60Sn35Sb5 and Bi60Sn35Ag5 developed through conventional melting and casting processes, were chemically characterized through plasma optical emission spectrometry, X-ray spectrometry, laser spectrometer, by optical microscopy. Tests were also performed to determine the Leeb hardness by the impact method.

The processing of the samples was quite difficult, due to their ductile nature, there were fine scratches left on the surface of the material. Even so, the formation of a homogeneous and well-defined structure, even almost eutectic, of the Bi60Sn40 and Bi60Sn35Sb5 alloys is highlighted, and lamellar-globular structure is observed, with compounds spread throughout the mass of the material for the Bi60Sn35Ag5 alloy. The intermetallic phases in lead-free solders are hard, this can also be seen from the hardness values, where sample 3 with 5%Ag has the highest values. These low melting alloys form either solid solution with each other or also form compounds phase. When they are in operation, these alloys can change their microstructure due to the changes that take place during the diffusion processes, at the same time the formation of compounds can potentially affect the microstructure, subsequent wetting behavior of substrates, and mechanical properties. These aspects need to be researched as thoroughly as possible.

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