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INVESTIGATION OF MULTICOMPONENT LEAD-FREE SOLDERS

According to the directives (RoHS and WEEE) adopted by the European Union, lead has been banned from the manufacturing processes because of its health and environmental hazards. Therefore, the development of lead-free solders is one of the most important research areas of the electronic industry. This paper investigates multicomponent Sn-Ag-Cu based lead-free solders with different compositions. The properties of the six-component Innolot (SAC+BiSbNi) and two low-Ag containing alloys were compared with the widespread used SAC307 solder. Microstructure investigations and X-ray diffraction measurements were performed to analyze and identify the formed phases, furthermore, tensile tests and microhardness measurements were executed to determine the mechanical properties of the examined solders.

Keywords: lead-free solder, multicomponent, microstructure, X-ray diffraction, mechanical properties

1. Introduction

The environmental impact of solder alloys is an important factor during manufacturing. Because of environmental reasons, the European Union issued the WEEE = Waste Electrical and Electronic Equipment and RoHS = Restriction of Hazardous Substances directives. These limit the use of certain hazardous substances, such as lead in electronic components. Therefore, the electronic industry has to switch to lead-free solder alloys from the conventional Sn-Pb alloys [1,2].

The Sn-Ag-Cu (SAC) alloys are the most commonly used lead-free solders. However, the available alloys cannot replace the well-proven Pb-containing alloys without difficulties which motivates the development of novel alloy types [3,4]. Our research focuses on the examination of a widely used solder alloy SAC307, a novel, 6-component alloy named Innolot (marked as "SAC307+BiSbNi ") and two not yet widely used solder alloys with decreased Ag content.

TABLE 1

Chemical composition of the solder alloys determined by ICP [wt.%]

Solder	Ag	Cu	Bi	Sb	Ni	Sn
SAC307	3.03	0.76	0.005	0.008	0.002	bal.
SAC307+BiSbNi	3.08	0.76	2.98	1.36	0.12	bal.
SACX0807+Bi	0.68	0.72	2.71	0.027	0.005	bal.
SACX+BiSbNi	0.47	1.35	4.29	2.68	0.19	bal.

The Innolot alloy (from now on SAC307+BiSbNi) is a modification of the widely used SAC307 alloy. As seen in Table 1, more additives – Bi, Sb and Ni – are added to the SAC system to improve the mechanical characteristics. Some part of Bi and Sb are in solution, while Ni improves strength by forming intermetallic compounds [5,6].

Due to the high Ag content of SAC307 and SAC307+BiSbNi alloys, their production is expensive. Therefore, solder alloy manufacturers aim to develop alloys with less Ag content [7]. The last two alloys in Table 1 are good examples for such an effort, which contain 0.7 and 0.5 wt.% Ag.

The objectives of the performed examinations are the following. To compare the SAC307 alloy with SAC307+BiSbNi, and to investigate how does the decreased Ag content affect the mechanical and microstructural properties of the examined alloys.

2. Experimental

The bulk solder materials were produced by Henkel Hungary Ltd. The bulk alloys were put in a ceramic crucible and melted in an electric resistance furnace at 400°C. After 15 minutes of isothermal holding, the melt was poured into a steel mould preheated to 200°C. After solidification, the die was disassembled and the ingots were removed. 5 tensile test specimens were casted from each alloy, while one sample was casted for X-ray diffraction (XRD) examinations.

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Samples were cut from the 11 mm diameter cylinder ingots for microstructure examinations that were mounted in Duracryl type resin. After standard metallographic sample preparations (grinding: P240, P320, P500, P800, P1200, P2000, P2400 and polishing: MD Mol and MD clothes using Lubricant Blue and a final polishing with 0.02 μm SiO_2 paste), microstructure examinations were carried out with a Zeiss AxioVision Imager m1M optical microscope and a Zeiss EVO MA10 scanning electron microscope (SEM), equipped with EDAX microprobe (EDX) [7]. An additional etching with 38% HF for 30 s was applied for SEM examinations.

Phase analysis was performed with a Phillips PW1830 type diffractometer equipped with a diffracted beam monochromator operating with CuKα radiation. Standard (DIN-EN-50125) tensile test specimens (Fig. 1) were machined from the ingots. An Instron 5982 type universal mechanical tester with 10 kN maximal force was used for the mechanical tests. Experiments were carried out at room temperature with 3 mm/minute speed which equals 10^{-3} s^{-1} strain rate.

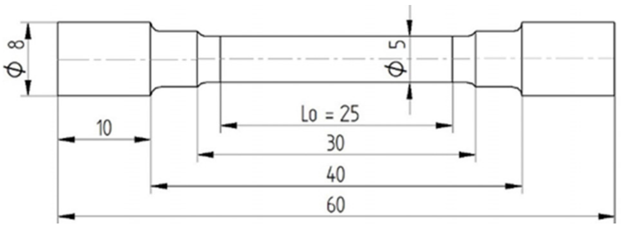


Fig. 1. The applied tensile test specimen

Vickers hardness was measured on the alloys with 0.3 kg load and 10 s indention time using an Instron Tukon 2100 B equipment. 10 parallel measurements were made for all alloy types.

3. Results and discussion

3.1. Microstructure

Fig. 2 shows the optical microscope images of the alloys. The SAC307, SAC307+BiSbNi and SACX0807+Bi alloys have hypoeutectic microstructures with β-Sn dendrites and different amount and types of eutectics. The SACX+BiSbNi alloy has hypereutectic structure consisting of primary $(Cu,Ni)_6Sn_5$ intermetallic compounds and different eutectics. This alloy clearly shows that this amount of Cu content increase and Ag content decrease cause dramatic changes in the microstructure. The large, coarse particles of primary $(Cu,Ni)_6Sn_5$ phase degrade the mechanical properties of the solder alloy [7].

The SEM images and measured compositions of the alloys are shown in Fig. 3. It can be concluded that the SAC307 consist of β-Sn solid solution and fine eutectic containing Ag and Cu. For the other three alloys, the Bi containing eutectic also appears due to the 3 and 4 wt.% Bi content. Particles of the (Bi) solid solution are clearly visible on the SEM images as white particles owing to its high atomic number. The individual phases of the eutectic are much better distinguishable on the SEM images, namely β-Sn solid solution and Ag_3Sn and $(Cu,Ni)_6Sn_5$ phases. Due to the high amount of Cu and Ni content, large primary $(Cu,Ni)_6Sn_5$ particles appear in the SACX+BiSbNi alloy.

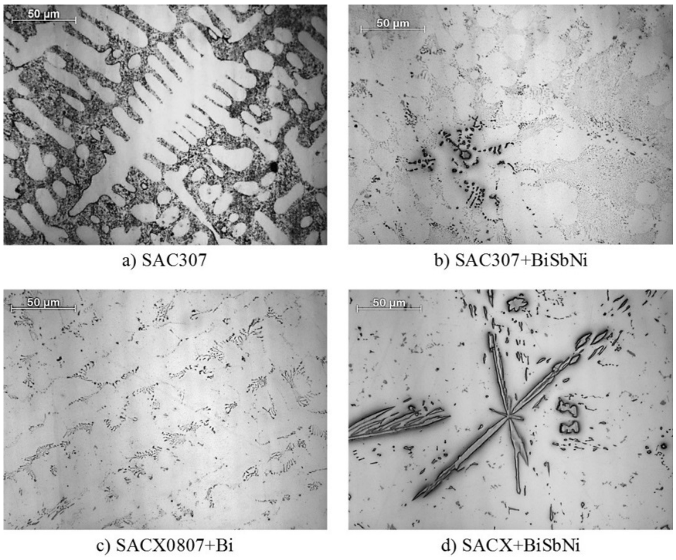
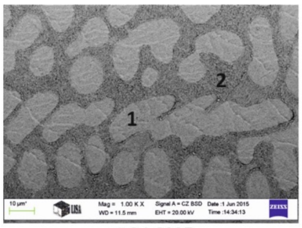
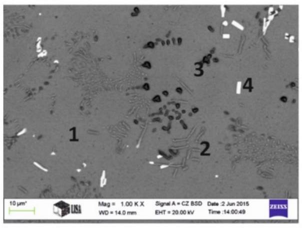


Fig. 2. Optical microscopic images of the examined solder alloys



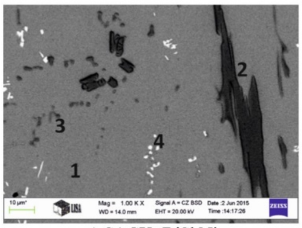
a) SAC307

Element	Analysed phases	
	1	2
	β-Sn	(β-Sn+ Ag_3Sn+Cu_6Sn_5)
Sn	99.50	87.85
Ag	0.50	7.48
Cu	-	4.67



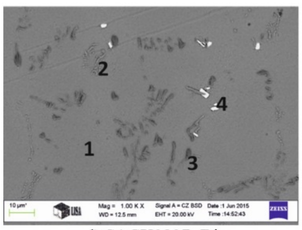
b) SAC307+BiSbNi

Element	Analysed phases			
	1	2	3	4
	β-Sn	Ag_3Sn	$(Cu,Ni)_6Sn_5$	(Bi)
Sn	95.05	30.93	51.58	15.13
Ag	0.25	66.33	-	-
Cu	-	2.74	41.19	-
Bi	2.89	-	-	84.87
Sb	1.81	-	-	-
Ni	-	-	7.23	-



c) SACX+BiSbNi

Element	Analysed phases			
	1	2	3	4
	β-Sn	$(Cu,Ni)_6Sn_5$		(Bi)
Sn	94.25	46.78	61.89	46.00
Cu	-	45.41	36.03	-
Bi	2.76	-	-	54.00
Sb	2.99	-	-	-
Ni	-	7.81	2.08	-



d) SACX0807+Bi

Element	Analysed phases			
	1	2	3	4
	β-Sn	Ag_3Sn	Cu_6Sn_5	(Bi)
Sn	96.09	49.35	71.17	34.02
Ag	0.65	50.65	-	-
Cu	1.12	-	28.83	-
Bi	2.14	-	-	65.98

Fig. 3. SEM images of the examined alloys and measured compositions (EDS, at.%) of the phases

3.2. Phase analysis

Fig. 4 shows the diffraction patterns of the examined alloys. The high intensity reflections correspond to the β-Sn phase, while those of the intermetallic compounds are marked. Reflections of the Ag_3Sn phase appear at 35,38,40,52,69,75,76°; those of the Cu_6Sn_5 phase are found at 43 and 60° and those of the Bi phase are at 28 and 38°. The Ag_3Sn and Cu_6Sn_5 phases were identified in all alloys, while $(Cu,Ni)_6Sn_5$ was found in the high Ni content alloy. The Ag_3Sn phase has higher intensity in the SAC307 and the SAC307+BiSbNi alloy, while those are smaller for the SACX+BiSbNi and SACX0807+Bi alloys. The intensities of the Cu_6Sn_5 reflections are similar for all four alloys. The Bi phase is present in all alloys except the SAC307. Similar intensities can be seen in the SAC307 and SAC307+BiSbNi alloys. The composition of SACX+BiSbNi alloy strongly differs from the previous ones, which is also visible on the XRD pattern as smaller intermetallic phase reflections and stronger Bi reflections. The pattern of the SACX+BiSbNi and the SACX0807+Bi alloys are similar.

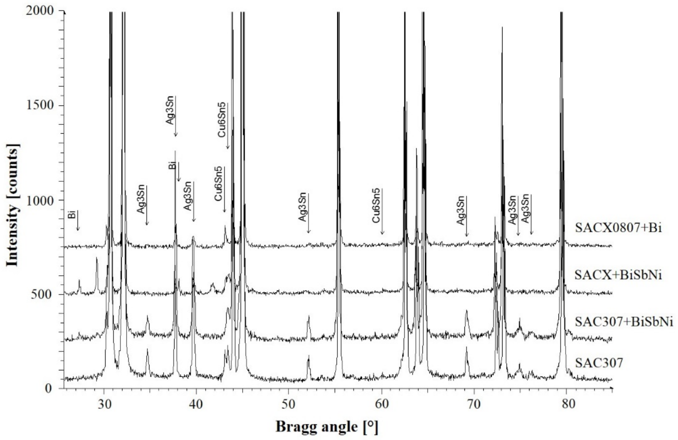


Fig. 4. XRD patterns of the examined alloys

3.3. Mechanical properties

Table 2. contains the results of tensile tests and hardness measurements. Figs. 5-8 show the yield strength (YS), ultimate tensile strength (UTS), elongation and Vickers hardness (HV) values. The UTS, 0.2YS and HV0.3 of SAC307+BiSbNi is about twice as large, and the elongation is around half as those of SAC307 due to the alloying elements. The UTS and YS of the low Ag alloys are between those of SAC307 and a SAC307+BiSbNi. From those, hypoeutectic SACX0807+Bi has lower UTS and YS and higher elongation compared to hypereutectic SACX+BiSbNi. SACX+BiSbNi has the smallest elongation from the examined alloys (Fig. 7). Fig. 9 shows one typical stress-strain curves of the alloys. The negative effect of lowered Ag content on the mechanical properties can be observed. The hardness values of the lowered Ag content alloys are similar to those of SAC307+BiSbNi alloy, which is not in agreement with the UTS and YS variation.

TABLE 2

Mechanical properties of the examined alloys

Solder	0.2YS [MPa]	UTS [MPa]	Elongation [%]	HV0.3
SAC307	46.54 ±1.29	39.03 ±1.47	35.59 ±4.79	15.7 ±0.5
SAC307 +BiSbNi	88.68 ±3.82	62.72 ±1.76	17.09 ±2.61	31.4 ±0.7
SAC0807+Bi	65.07 ±0.64	44.34 ±0.95	12.50 ±2.42	30.0 ±2.1
SACX +BiSbNi	75.62 ±4.48	52.26 ±1.05	7.48 ±2.64	32.2 ±0.7

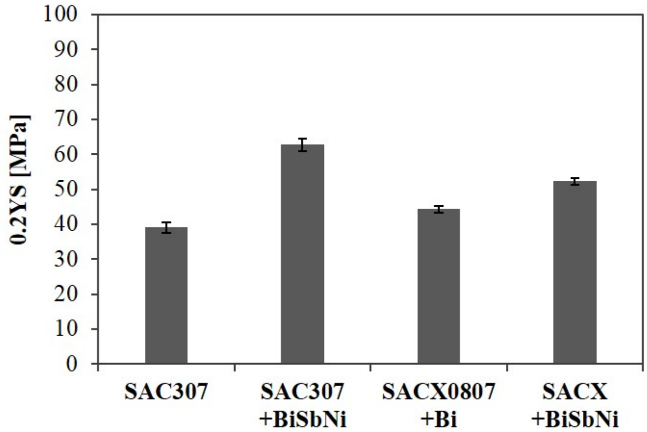


Fig. 5. Yield strength of the examined alloys

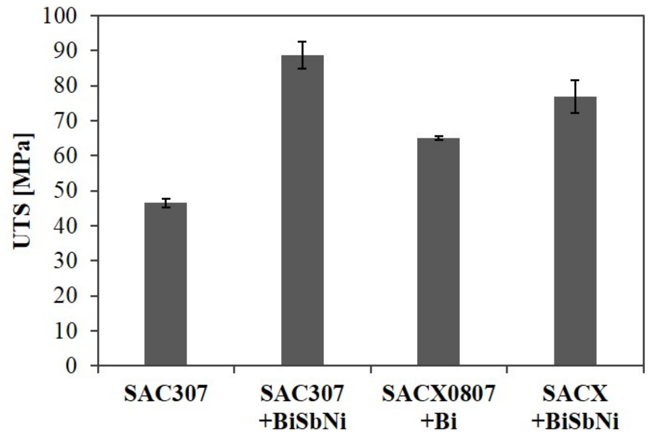


Fig. 6. Ultimate tensile strength of the examined alloys

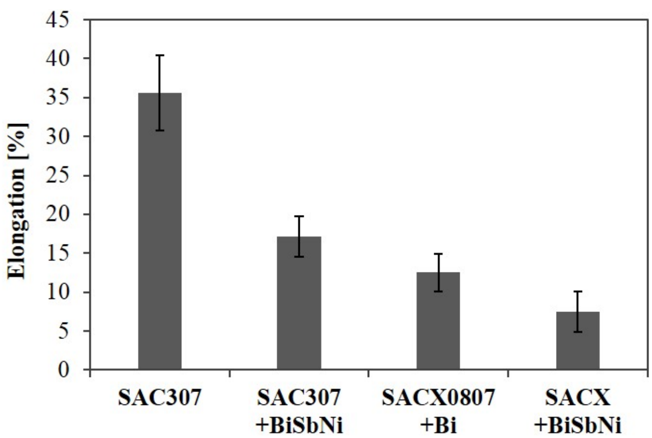


Fig. 7. Elongation of the examined alloys

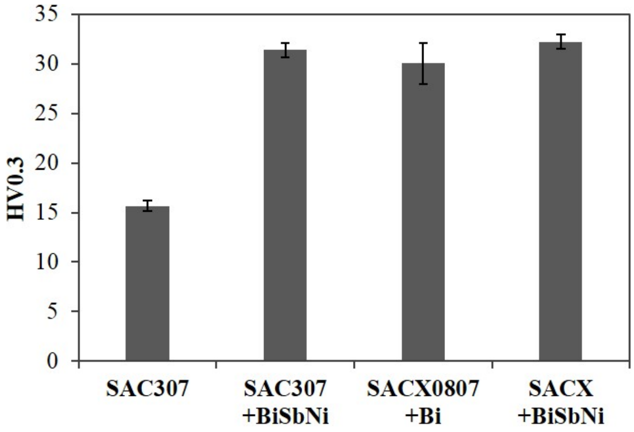


Fig. 8. Hardness of the examined alloys

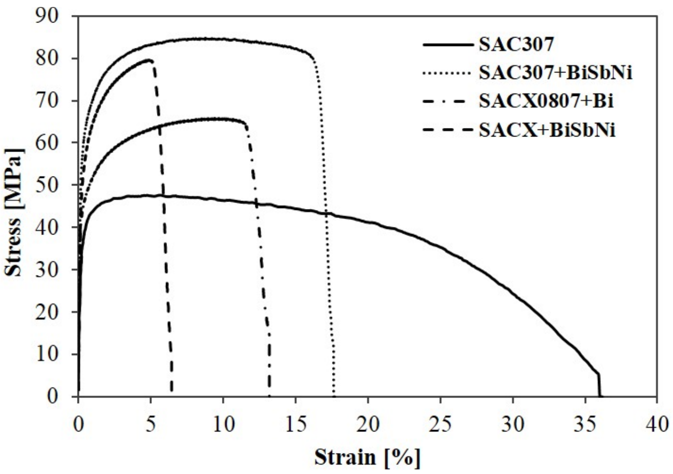


Fig. 9. Typical stress-strain curves of the examined alloys

4. Conclusions

The microstructural and mechanical properties of multi-component, lead-free Sn-Ag-Cu based solder alloys were investigated. The following conclusions were deduced:

1. Due to the higher Ag content, larger amount of intermetallic compounds were formed in the SAC307 and SAC307+BiSbNi alloys. The Bi is present in the form of solid solution of the eutectic in the examined Bi-containing alloys. $(Cu,Ni)_6Sn_5$ intermetallic compounds are also present as primary phases in the SACX+BiSbNi alloy.
2. The ultimate tensile strength, yield strength and hardness of the SAC307+BiSbNi alloy are around twice as those of SAC307, and its elongation is about half of that of SAC307. The ultimate tensile strength values of SACX+BiSbNi and SACX0807+Bi alloys are in between those of SAC307 and SAC307+BiSbNi, and SACX+BiSbNi has the lowest elongation. These differences are due to the strength increasing effect of the intermetallic compounds and Bi which was revealed by the microstructure examinations.

Finally, if higher strength is required, SAC307+BiSbNi (Innolot) performs the best from the examined alloys, on the other hand, if higher elongation is desired, SAC307 performs the best. If cost efficiency is of major importance, SACX0807+Bi could be the best choice.

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