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EFFECT OF SILVER CONTENT ON THE PROPERTIES OF LEAD-FREE SOLDERS

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According to the new RoHS Directive 2011/65/EU of the European Union on the restriction of hazardous materials for environmental reasons, the application of lead-containing solders in electronic devices should be avoided. It follows that Hence, there is an increased interest in lead-free solders to ensure the reliable operation of electronic devices under extreme conditions (e.g. high temperature, vibration) and to overcome/surpass the limits of resilience in lead-containing solders [1].We studied the relationship between silver content (1%, 2%, 3%, 4%) and the structural-mechanical properties of SAC alloys.
Keywords: soldering alloy, lead-free, SAC

Introduction

As of July 1, 2006, it is forbidden to use lead-containing solders in the production of electronic devices. Electronic products to be installed in vehicles are exempt on a temporary basis. Even though lead-free solders are long since known in production technology, eutectic tin-lead solders – already used some thousand years ago – have undoubtedly taken the leading role and become widespread in the production industry. With lead being phased out, there is, however, a strong interest in lead-free solders, particularly in eutectic Sn-Ag and Sn-Ag-Cu (SAC) alloys. Instead of 183 °C, that is the melting point of the eutectic Sn-37% Pb alloy, these materials have a melting point of approx. 221 °C. This property allows for higher application temperatures [2]. Newly introduced lead-free solders have to comply with several application requirements such as: no substances potentially harmful to human health are contained; long-term availability of material components; material compatibility with the technologies and electric components currently in use; easy solvability of repair issues, price competitiveness and comparability to that of Sn/Pb alloys [3].

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Out of SAC alloys, alloys with nearly eutectic composition containing 3.0 to 4.0 weight% silver and 0.5 to 1.0 weight% copper are the most common [1, 2]. *Che* et al. [4] studied a SAC alloy with 1%, 2% and 3% silver, with particular emphasis on the relationship of silver content and mechanical properties such as elongation, conventional yield strength and tensile strength. They determined that higher silver content is associated with higher strength. Increased silver content reduces the formability of solder joints and consequently shortens the service life of electronic components. This statement corresponds to the test results reported by *Amagai*, M. et al. [5]. Accordingly, materials with low silver content are targets for use wherever possible. The silver content of the alloy clearly affects the volume fraction of the Ag_3Sn intermetallic phase formed and the size of tin grains. As a result at elevated Ag levels, a well-dispersed intermetallic phase and small tin grain size can be detected in the microstructure of the solder, which allows for higher strength properties strength and higher resistance to fatigue. All this is confirmed by *Terashima* et al. [6] who, based on the results of thermal fatigue examinations stated that solders with higher silver content have a higher fatigue life.

1. Experimental

The studied samples involved commercially available and widely used SAC105, SAC205, SAC305 and SAC405 solders. For the preparation of the test pieces, two kinds of mold were used, as shown in Figures 1 and 2. The first mold (*Figure 1*) is appropriate for the casting of a cylindrical body, which can be processed into a standard (DIN-EN-50125) tensile test piece. The second (*Figure 2*) is suitable for the preparation of coin test pieces that are used for microscopic examination and hardness tests.

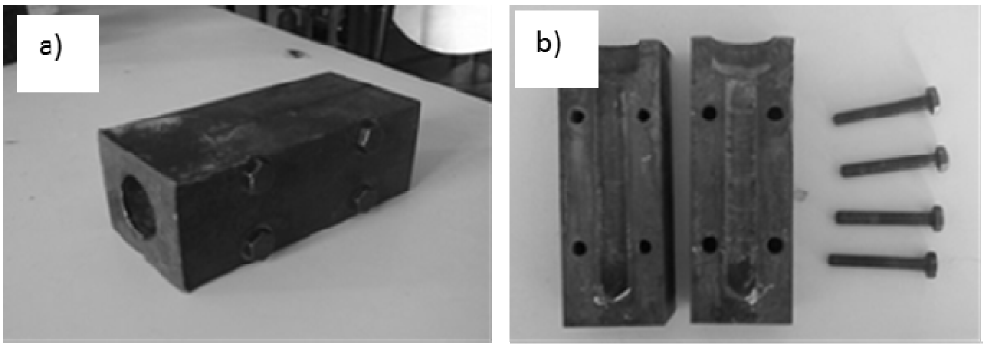

Figure 1. Mold for tensile test pieces before casting (a) and dismantled (b)

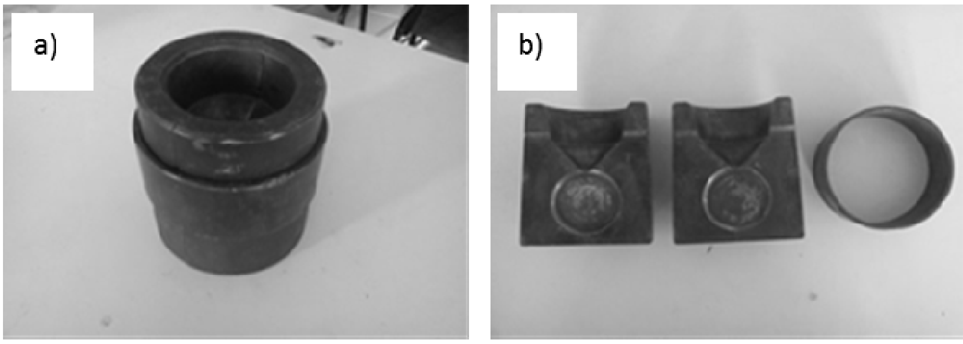

Figure 2. Mold for coin test pieces before casting (a) and dismantled (b)

The melting and casting parameters for the casting process were the following.

Table 1

Melting and casting parameters

Parameter	**Value**
Melting temperature	350 °C
Mold preheating temperature	230 °C
Holding time before the first casting	30 min
Melting time for the second and third casting	10 min
Mold preheating time for the first casting (minimum)	1 hour
Mold preheating time for the second and third casting	7 min

As-cast pieces are shown in *Figure 3*.

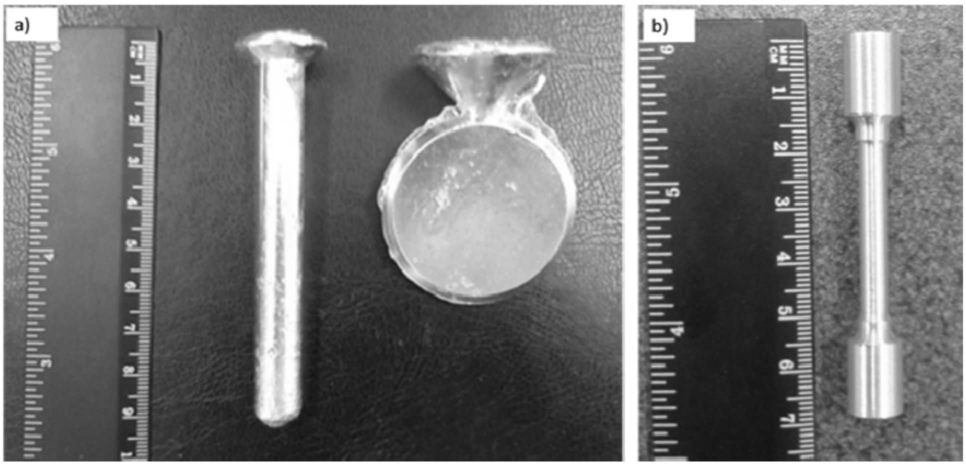

Figure 3. Casted tensile test piece and coin test piece (a), machined tensile test piece (b)

The chemical composition of the studied specimens (Table 2) was determined using inductively coupled plasma (ICP) spectrometry.

Table 2

Composition of the studied solders

Specimen ID	Elements (%)						
	Sn	Ag	Cu	Bi	Pb	Sb	Zn
SAC105	98.3273	1.15	0.514	< 0.005	0.0015	0.0011	0.0011
SAC205	97.2499	2.21	0.511	0.0010	0.0012	0.0167	0.0102
SAC305	96.156	3.35	0.485	< 0.005	0.0020	0.0012	0.0008
SAC405	95.1727	4.28	0.536	< 0.005	0.0032	0.0013	0.0018

2. Results

The proper preparation of test pieces (from solders) is a necessary prequisite for optical microscopy analysis. For specimen grinding, SiC abrasive paper was used. In this case, the grinding step was completed with the application of P1000 grade abrasive paper. Grinding was followed by polishing, where the specimens were subject to surface modification by various grade cloths and diamond suspensions of various particle size. Polishing started with woven cloth and a 9 μm diamond suspension, then a 3 μm suspension. Next, fleecy cloth was applied with a 3 μm diamond suspension again. Eventually, final polishing was performed using colloidal silica gel on a fleecy cloth. Colloidal silica gel contains negatively charged SiO_2 parts of a pH between 8 and 11, which softly etches the surface of the specimen, therefore the primary ß-Sn dendrites and the Sn-Ag_3Sn and Sn-Cu_6Sn_5 eutectics between dentrites could be made clearly visible in the studied specimens.

Optical microscopy analyses were carried out using a Zeiss Observer Z1m light microscope and AxioVision Rel. 4.8 software. *Figure 4* presents the optical micrographs of the ground-polished specimens at a magnification of 100x. The micrographs affirm the observations described in the literature about the scarce appearance of tiny Ag_3Sn intermetallic particles besides relatively large primary ß-Sn grains in the solder matrix of SAC105 (solders). A smaller quantity of primary ß-Sn dendrites are present in the SAC205 specimen, surrounded several tiny Ag_3Sn intermetallic particles in a random pattern. In the SAC305 alloy, Ag_3Sn forms a connected network around the primary ß-Sn. Here, primary ß-Sn grain size is, again, much smaller. In the SAC405 solder, the Ag_3Sn intermetallic particles are well-dispersed in the matrix, with the lowest inter-particle distances and the poorest quantity of primary ß-Sn grains.

To determine the surface area share of primary ß-Sn in the specimens, 20 visual fields were examined for each specimen using digital image analysis with AxioVision imaging software. The optical micrographs of SAC105 and SAC205 specimens were captured with bright-field illumination, then measurements were carried out (on these micrographs) by means of the AxioVision imaging software. This software offers the possibility of gray and binary image transformations. First, contrast and brightness adjustment was applied to the gray image, then noises were removed using sigma filter. Subsequently, the objects were separated from the background (i.e. detection). In the binary image generated so, the tiny undetected areas were added to the detected objects using the so-called „Fill Holes" operation. Next, computational measurements were carried out. In case of SAC305 and SAC405 specimens, white light illumination was insufficient, thus, a dark field contrast procedure was applied. In doing so, we obtained images of proper quality for the digital image analysis whereby the primary β-Sn was distinguishable from the Sn-Ag_3Sn and Sn-Cu_6Sn_5 eutectics. The measurement was basically performed in a way similar to the previous two cases. The micrographs captured by the AxioVision imaging software with dark field illumination were passed on to contrast and brightness adjustment then filtering (Sigma filter). Following this, detection was performed and the unwanted detected objects were removed, finally measurements were executed. *Figure 5* shows the measurement results clearly confirming the observations from the optical micrographs, namely: with the increase of silver content, the surface area share of eutectic increases.

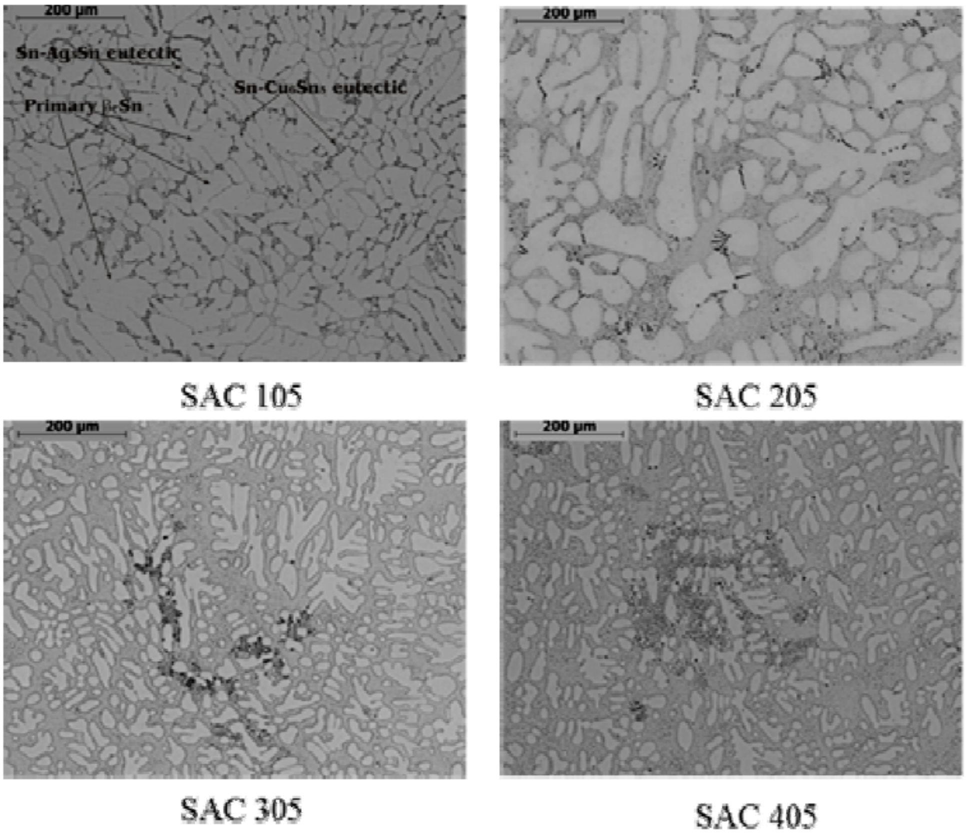

Figure 4. Optical micrographs of SAC 105, SAC 205, SAC 305 and SAC 405 specimens (original magnification: 100x)

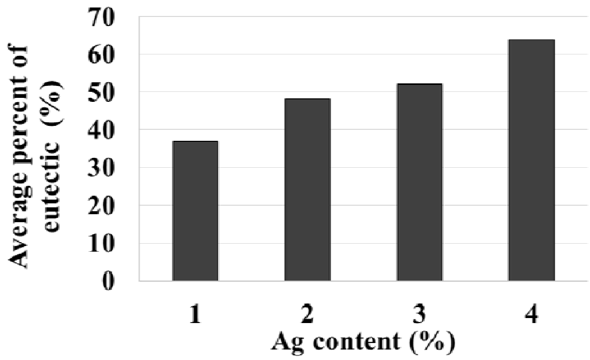

Figure 5. Variation of the surface area share of eutectic determined by digital image processing vs. silver content

Microhardness tests were performed using an Tukon 2100B apparatus, which operates on Vicker's principle. The analysis required ten measurements per specimen, with a load of 0.5 kg and a load time of 10 s.

The results of microhardness testing can be seen in *Figure 6*. Observably, as the silver content increases, the hardness of the solder rises, which is probably due to the growing number of Ag_3Sn intermetallic particles formed in the bulk material.

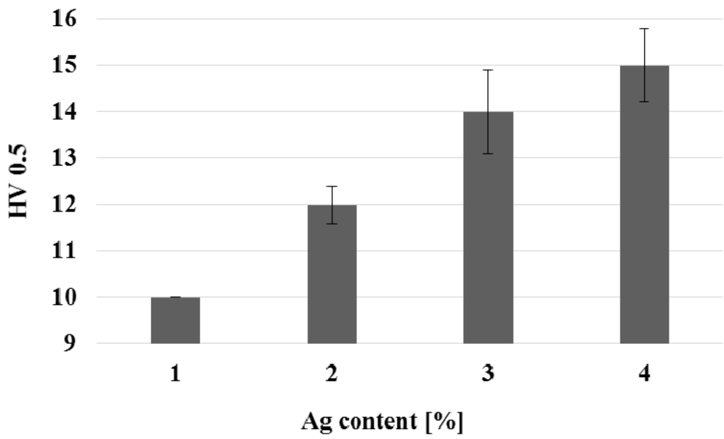

Figure 6. Variation of microhardness test values vs. increasing silver content

Tensile tests were performed at room temperature using an Instron 5982 type universal material testing machine, with a tensile speed of 3 mm/min. Based on the tensile test results (*Figure 7*) it can be stated that both tensile and yield strength rises with increasing silver content, except for the SAC405 specimen, where there is a minimal decline in yield strength compared to the SAC305 specimen.

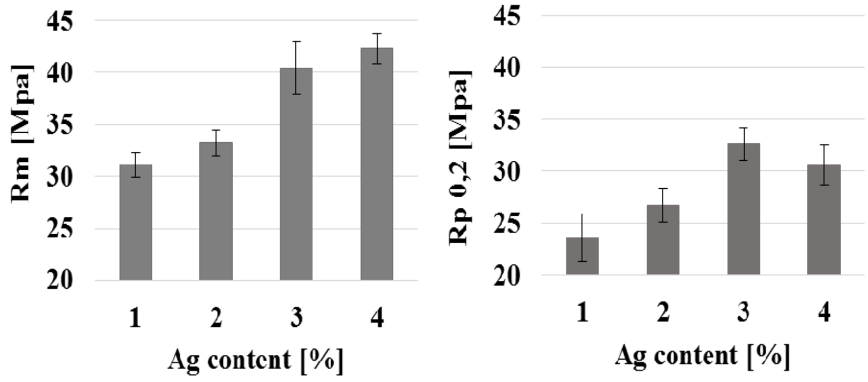

Figure 7. Variation of tensile strength and conventional yield strength values vs. increasing silver content

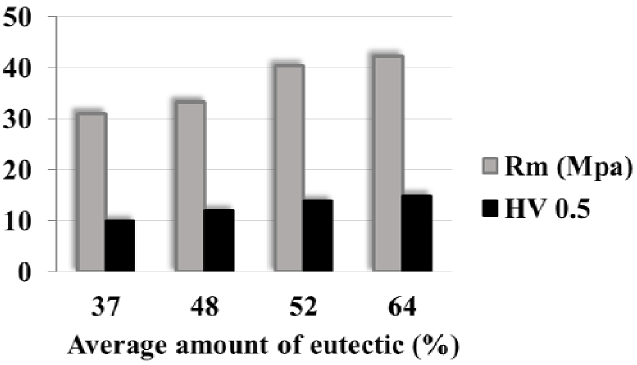

Figure 8. Effect of the quantity of eutectic on the studied parameters

Summary

In this paper, we studied the variation of microstructural and mechanical properties of SAC (Sn-Ag-Cu) lead-free solders vs. silver content (1%, 2%, 3%, 4%).

Based on the image analyses of optical micrographs it can be concluded that in the bulk material of lead-free SAC alloys, the quantity of Ag_3Sn rises with the silver content. Higher silver content results in an increased number of Ag_3Sn intermetallic particles and the reduced formation of primary ß-tin. It follows from this and the results of mechanical tests that the presence of small intermetallic particles improves the strength of solder. Therefore, both the Young's modulus and yield strength increase. The increase in the quantity of eutectic leads to also higher hardness values, which are confirmed by results in the professional literature [1–6] as well.

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