THERMAL EXPANSION OF Cu-Ga-Sn ALLOYS

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ABSTRACT

The thermal and microstructural properties of five copper-gallium-tin alloys (Cu-Ga-Sn) and two important intermetallic compounds Cu\textsubscript{3}Sn and CuGa\textsubscript{2} have been investigated by dilatometry, scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction. The temperature dependence of thermal expansion and coefficient of linear thermal expansion (CLTE) were obtained.

Introduction

Copper-gallium-tin alloys (Cu-Ga-Sn) are applied in the industry as diffusion-hardening solders (DHS) and dental filling materials. The low melting temperature of gallium allows using it as a liquid component at mixture with solid metal. Preparation of these restorative materials involves mixing a metallic powder and a gallium-based liquid. The total setting reaction has two components and may be written as follows:

\[ \text{Cu}_3\text{Sn} + \text{Ga} \rightarrow \text{CuGa}_2 + \text{Sn} \] (1)

The reaction between gallium and the Cu\textsubscript{3}Sn powder particles leads to the formation of two intermetallic compounds Cu\textsubscript{3}Sn, CuGa\textsubscript{2} and Sn-rich phase. Since the powder particles are incompletely consumed during solidification. Formation of these reaction phases is a difficult process and takes place in several stages with the formation of intermediate compounds. The course of the reaction of liquid gallium with copper and tin by diffusion hardening was extensively studied in work [1]. The mechanical properties and setting dimensional changes [2-4], handling characteristics [5,6], corrosion characteristics [7] and microstructure [8,9] of alloys based on gallium have been reported.

In addition, Cu\textsubscript{3}Sn is an important intermetallic compound (IMC), which commonly forms during interface reactions between most Sn-based solders and Cu substrates [10]. Intermetallic compounds can also grow at the interface of the solder and the substrate during storage [11] at ambient temperatures. The continuous performance demands and minimization of modern electronic products have led to an increased current and accompanying Joule heating. If all of the components within the device have identical coefficients of thermal expansion (CTE), and heat transfer is instantaneous, then they will expand and contract at the same rate, and no thermally induced stress will arise. Therefore, the thermal expansion of Cu\textsubscript{3}Sn and CuGa\textsubscript{2} plays an important role in the thermal fatigue of Cu-Ga-Sn solder joints.

Experimental

The Cu-Ga-Sn alloys were prepared by diffusion hardening from the prepared paste. The initial paste composition was the following (wt.%): Cu-40, Ga-31, Sn – the rest. Cu\textsubscript{3}Sn powder consisted of spherical particles (fraction: – 40 µm). Tin powder also included spherical particles of the same size. The mix of these powders with gallium powder (particles size less than 500 µm) was shaken very intensively in polyethylene capsules using special mixer. Then the paste prepared was placed into the form and tightened before solidification. The samples hardened were of cylindrical shape.
with the diameter 10 mm and height 3-4 mm. Samples could not be polished with good quality after 1 h ageing since they had only about 20% of maximal hardness. Five specimens were prepared for dilatometry analyses.

Cu$_3$Sn and CuGa$_2$ intermetallic compounds were prepared from pure gallium (99.999 %), copper (99.95 %) and tin (99.99) induced by double arc melting in a high-purity helium atmosphere.

Thermal expansion of copper-gallium-tin alloys (Cu-Ga-Sn) and intermetallic compounds Cu$_3$Sn and CuGa$_2$ was investigated on the NETZSCH DIL 402C dilatometer using high-sensitive detector (linear variable displacement transformer - LVDT). The experiment was carried out in the high-purity helium atmosphere. The heating speed was constant and equal to 2 K/min. The instantaneous coefficient of linear thermal expansion ($a$, CLTE) at a temperature T was calculated from the ∆L versus temperature curves by means of the numerical derivative of the ∆L(T) curve according to Eq. (2). The accuracy of the CLTE(T) values is within ± 0.5 ppm·K$^{-1}$.

$$a(T) = (1/L_0) \cdot (∆L/∆T).$$  \hspace{1cm} (2)

The XRD patterns were obtained using a D8 ADVANCE X-ray diffractometer with CuKα radiation, β-filter and super speed VÁNTEC-1 detector. Analysis of phase composition and crystallographic characteristics calculations were performed using software DIFFRAC plus [12,13] and database of the International Centre for Diffraction Data PDF4+[14]. Scanning electron microscope Carl Zeiss EVO 40 equipped by the EDX system Oxford Instruments INCA X-Act was used to perform the investigations.

**Results**

**SEM/EDX and XRD measurements.** Cu-Ga-Sn alloys have a structure with many phases. Using SEM and EDX analyses, the structure can be described as consisting of a white regions (composition wt%: Cu-(1-2), Ga-(5-7), Sn – the rest) and a dark regions (composition wt.%: Cu-(31-33), Ga – the rest). Further, the solidified Cu-Ga-Sn samples were well polished after ageing. These metal composites show a complex structure including three main phases: Sn-rich phase, CuGa$_2$ crystals and Cu$_3$Sn particles (Fig. 1).
Fig. 1. SEM image of hardened paste specimen (polished), back scattering detector. White field - Sn-rich phase, black field – CuGa₂ crystals; gray disks – Cu₃Sn particles cross-sections. Results of the XRD characterization of Cu₃Sn and CuGa₂ are presented in Figures 1-2 and Table 1. According to XRD analysis intermetallic compounds are single phase.

Fig. 2. Diffraction patterns of sample CuGa₂. The figure shows the results of full profile analysis of diffraction patterns: experimental (solid line), calculated (open circles), difference curve, and as well as a bar-diagram.

Fig. 3. Diffraction patterns of sample Cu₃Sn. The figure shows the results of full profile analysis of diffraction patterns: experimental (solid line), calculated (open circles), difference curve, and as well as a bar-diagram.
Table 1. Lattice parameters, cell volumes, Bragg R factor and space group of intermetallic compounds Cu$_3$Sn and CuGa$_2$.

<table>
<thead>
<tr>
<th>Phase name</th>
<th>CuGa$_2$</th>
<th>Cu$_3$Sn</th>
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</thead>
<tbody>
<tr>
<td>R-Bragg</td>
<td>0.669</td>
<td>0.647</td>
</tr>
<tr>
<td>Space group</td>
<td>P4/mmm</td>
<td>Cmcm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lattice parameters</th>
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<tbody>
<tr>
<td>a, nm</td>
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<tr>
<td>b, nm</td>
</tr>
<tr>
<td>c, nm</td>
</tr>
<tr>
<td>V, nm$^3$</td>
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</tbody>
</table>

**Dilatometry measurements.** Dilatometric curves of samples Cu-Ga-Sn in solidified condition are shown in Fig. 4. The change in length ($\Delta$L) of the samples with respect to its initial length $L_0$ is recorded with time for a constant heating rate of 10K·min$^{-1}$, from which the length $\Delta$L/$L_0$·$10^{-3}$ vs. T is plotted. One can see that the sample length changes monotonously at heating. This fact shows the absence of phase transitions in the temperature interval studied.

Fig.4. Dilatometric curves for five samples Cu-Ga-Sn (sample number is listed on the graph in brackets).

The results of calculation of CLTE the Cu-Ga-Sn samples in the temperature range 25-140 °C are presented in the histogram (Fig. 4).

In addition, the thermal expansion and CLTE of Cu$_3$Sn and CuGa$_2$ were investigated in the solid state (Fig. 5). According to SEM and EXRD analyses, as a result of solidification, intermetallic compounds Cu$_3$Sn and CuGa$_2$ are formed in the Cu-Ga-Sn alloys. Thus, it was necessary to carry out study of CLTE the systems Cu$_3$Sn, CuGa$_2$ and to establish their contribution to the thermophysical properties of Cu-Ga-Sn. Thermal expansion coefficients for the studied compounds are close to each other and equal to 19.2·10$^{-6}$·K$^{-1}$ for CuGa$_2$ and 18.34·10$^{-6}$·K$^{-1}$ for Cu$_3$Sn between 25 and 140 °C.
Fig. 5. Dilatometry curves for CuGa\textsubscript{2} [1] и Cu\textsubscript{3}Sn [2]

Fig. 5. Experimental CLTE values for five samples Cu-Ga-Sn in range 25-140°C

The difference in the CTE of alloy Cu-Ga-Sn and intermetallic compounds is caused by the presence of a solid solution of gallium in tin (about 5-7 of the masses.% Ga, Sn - rest), as well as the uneven distribution of spherical particles Cu\textsubscript{3}Sn in the alloy.

Summary

Most of the solder alloys have CTE in the low 20·10\textsuperscript{-6}·K\textsuperscript{-1} range with the exception of Bi-42Sn, which has a CTE of 15·10\textsuperscript{-6}·K\textsuperscript{-1}. Cu (used as lead frames) and FR-4 (the most common printed circuit board material) have CTE 16-18·10\textsuperscript{-6}·K\textsuperscript{-1} and 11.0-15.0·10\textsuperscript{-6}·K\textsuperscript{-1}. Therefore, if CTE of soldiers and components of printed circuit boards are essentially different, such as solder materials used does not seem possible. The Cu-Ga-Sn alloys can be used as solders for soldering copper.
products because they have similar values of CTE with copper. The measured mean value is \((18 \pm 2) \times 10^{-6} \cdot K^{-1}\) between 25 and 140 °C.

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References


