SEM study of a model system for Pb-free nanoparticle solders

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The production of electronics cannot be possible without soldering process. It is well known for a long time that the classical solders based on lead and tin represent a serious health risk and environmental problem. Hence there is a strong drive to find lead-free alternatives. Since 2003, a request for lead-free solders was implemented into the EU legislation. The regulations came to force in 2006. While they currently exempt high-Pb solders used as component solders and die attaches for automotive and other high temperature applications, there is a strong drive to find Pb-free alternatives for these high temperature electronic applications, as well [1]. The introduction of lead-free solders is associated with practical difficulties as there is no single replacement for the lead containing alloys, which would cover all technical applications. Lead-free solders presently used have often reliability problems, usually caused by worse mechanical properties, higher tendency to oxidation, higher occurrence of undesirable intermetallic phases and higher melting temperature T_m . They are generally either more expensive (e.g. Sn-Ag based solders) or their use leads to higher technology expenses.

Melting temperature of a solder is of the primary concern for both economical and technological reasons, as higher temperature means higher risk for the electronic components and boards. The melting temperature of classical Sn-Pb solder is as low as 183°C. Several eutectic lead-free solder systems try to approach this point (e.g. Sn–Cu: 227°C, Sn–Ag–Cu: 217.5°C, Sn–Ag–Bi–In: 210°C, Sn–Zn–Bi: 193°C). Hunting for low meeting points seriously limits the range of candidates amongst low toxic species. A promising approach in lowering meeting points is the use of solder pastes [1,2]. They contain powders of Pb-free alloys, which decrease their melting point in comparison with the corresponding bulk materials [3–6].

In this work, we studied the effect of lowering melting point of a material suitable as a candidate constituent for new solders, namely silver. The melting point of bulk silver is 962°C (which is far too high even in a category of high-temperature solders, defined by $T_m \ge 230^{\circ}C$ and limited usually by about 350°C due to polymer materials in substrates used in electronic industry).

Copper disks 6 mm in diameter were polished; a layer of silver powder was evenly spread over one of them and covered by another one. This set was put in a clamp and annealed at 400°C for 1 hour and for 3 hours. Metallographic cross sections were prepared from both samples and studied using a JEOL JSM 6460 scanning electron microscope (SEM) with Oxford Instruments INCA Energy analyser.

The results demonstrate that for powdered Ag the temperature 400°C is sufficient to produce a continuous Ag layer. Figure 1 compares samples annealed for various times. Shorter annealing time of 1 hour still leaves high density of pores in some regions of Ag layer (see Figure 1a), whereas 3-hour annealing produces a compact Ag layer without pores

(Figure 1b). A transition layer is observed in both samples at the Cu-Ag interface, the thickness of which increases with annealing time. An EDX linescan across the joint (see Figure 2) shows the increased amount of oxygen in the transition layer, hence the resulting structure can be described as Cu |Cu-O |Ag. Repeated linescans in both samples reveal a small local maximum of Ag concentration at the Cu |Cu-O interface. Small Ag particles and interfacial cavities are also frequently found at that region.

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Figure 1. SEM micrographs of cross sections (backscatter electron images). Samples were annealed at 400°C for 1 hour (a) and 3 hours (b).



Figure 2. SEM micrograph of sample annealed 1 hour at 400° C – a detail of the Cu | Cu-O | Ag transition region. EDX linescan was performed along the vertical line marked in the image (upper point of the scanned line corresponds to the left side in the plots of X-ray counts).