Developing new joining materials for low-temperature electronics assembly

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New regulations due to environmental and health concerns including the European RoHS (Restriction of Hazardous Substances) and WEEE (Waste Electric and Electrical Equipment) directives have led to a shift towards tin-based, lead-free solders in electric and electronic equipment. For the assembly of electronic devices on printed circuit boards (2nd level packaging), the most widely used lead-free alloy is near eutectic tin-silver-copper (Sn-Ag-Cu or SAC). Compared to tin-lead based solders, the higher melting points of SAC solders can result in additional stress, accelerated ageing and a global decrease in reliability for components and polymer-based printed circuit boards during reflow processing. These recent concerns have led to new research and development in lead-free solders area [1]. Numerous new alloy compositions are being investigated as well as new approaches like manufacturing alloy nanoparticles or improving mechanical properties with nanoparticle reinforcements in conventional micrometre-sized solders.

The present work focuses on a new kind of lead-free joining method for surface-mount technology based on precursor chemistry. The interest of metal oxalates as new soldering materials for die attachment (1st level packaging) was previously demonstrated with silver oxalate [2], [3]. The thermal decomposition of metal oxalates under controlled atmosphere can be used to produce small metal particles below their melting point. These particles are found to be in a highly active particulate form [4]. First experimental studies are focusing on several metal oxalates (tin oxalate and bismuth oxalate) to assess their suitability for low-temperature metal particle production. The main work is dealing with controlled chemical precipitation synthesis and characterization of the compounds (Figures 1 and 2) as well as study of the properties of decomposition solid products (powder X-Ray diffraction, Fourier-transform infrared spectroscopy, Scanning Electron Microscopy and thermal analyses under different atmospheres).

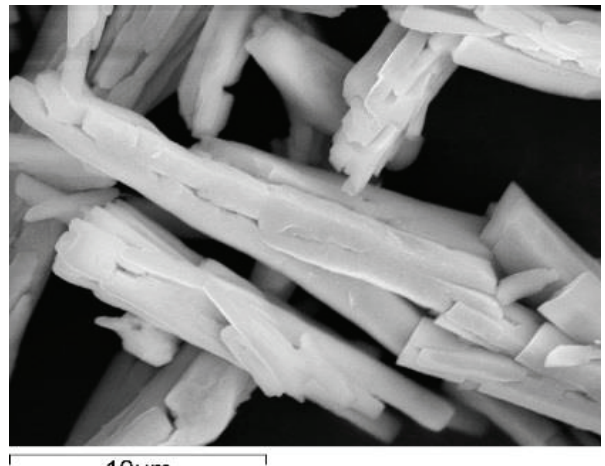

Figure 1 : Tin oxalate particles (SEM image)

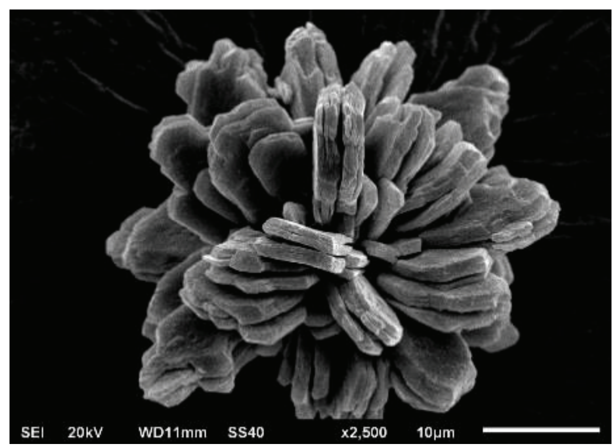

Figure 2 : Bismuth oxalate particles (SEM image)

First results tend to show that tin oxalate starts to decompose at about 573K. This temperature is too high to use as-precipitated tin oxalate for a soldering application at low temperature. Moreover, tin oxalate spontaneously decomposes into tin oxide even if the heat treatment is carried out under pure hydrogen. Small tin particles were though obtained from tin oxide under such reducing conditions close to 673K (Figure 3). The oxalate route could then be a way to produce morphology-controlled tin particles. Concerning bismuth oxalates, the first part of the work implied the precise control of the synthesis. Indeed, several hydrated oxalates and hydroxyl oxalates are known and their formation is strongly dependent on the synthesis

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parameters. Thermal analysis showed that dehydration of hydrated bismuth oxalate $Bi_2(C_2O_4)_3,7H_2O$ occurs in two steps between 303K and 473K. Then, under an inert atmosphere, bismuth oxalate decomposes into temporary nanometric bismuth metallic particles in between 483K and 523K (Figures 4 and 5). This range of temperature is below the melting point of bulk metallic bismuth ($T_m(Bi)$ = 544K). It is then possible to measure by differential thermal analysis the melting point of the nanometric bismuth particles formed. This characteristic and the sintering propensity of the nanometric metallic particles are currently being finely studied with the aim of potential use of a bismuth oxalate for soldering applications at low temperature.

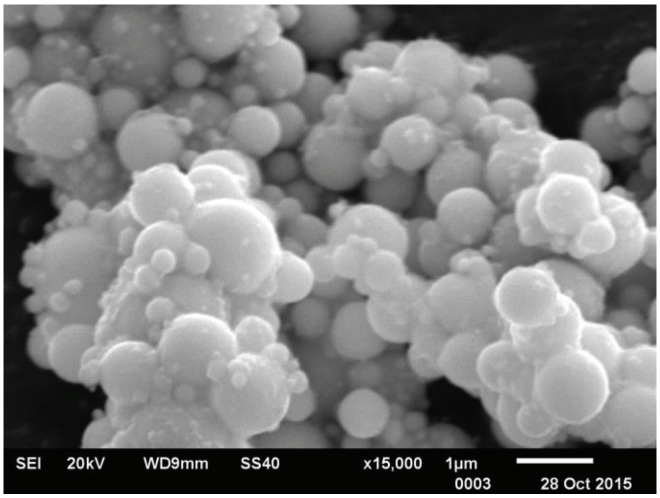

Figure 3 : Tin particles resulting from tin oxalate decomposition under hydrogen atmosphere

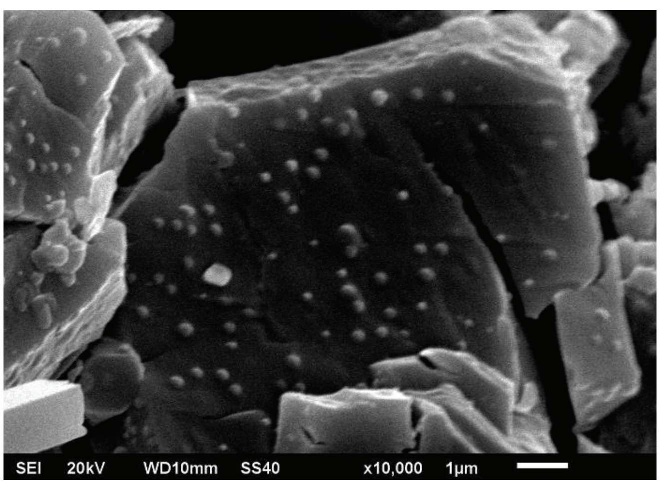

Figure 4 : Bismuth particles resulting from bismuth oxalate partial decomposition under nitrogen atmosphere

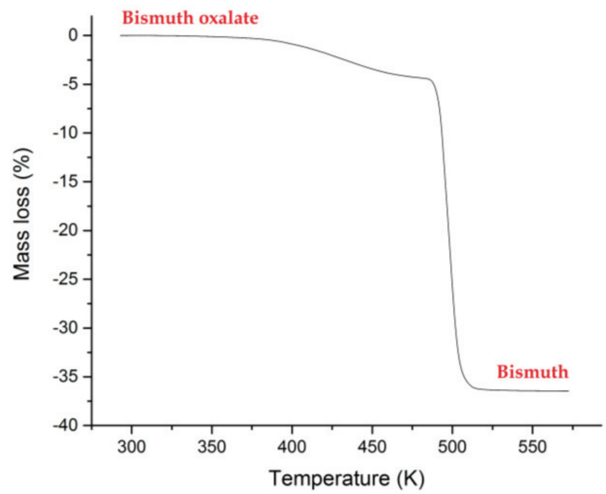

Figure 5 : Bismuth oxalate decomposition into bismuth (thermal analysis under nitrogen)

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