EU legislation requires that lead and other critical alloying elements have to be removed or replaced by non-hazardous element in the certain segments of the soldering technology. The mechanical and thermal properties, such as tensile strength and melting point, of the newly developed lead-free solder alloys differ significantly from the previously used lead-tin solders. Nowadays researchers deal with nanostructured solders that are capable of changing these properties.

The melting point of the solder can be reduced by paste solder from metal nanoparticles and the mechanical properties can be improved by a non-soluble nanoparticle-reinforced nanocomposite solder. The results of research on nanostructured solders are collected in this review.

**Keywords:** lead-free solder, composite, nanoparticles

### Introduction

Till now the most successful solder alloys were tin-lead (Sn-Pb), which has appropriate chemical, physical and thermal properties. These properties result in a good bond between the solder and substrate [1].

Different alloying elements can be used to improve the mechanical properties of lead-free solder, i.e. silver [2] or nickel [3]. Nickel can improve the mechanical properties by reducing the thickness of the Cu₃Sn intermetallic (IMC) layer on the interface of the solder/substrate [3]. The wettability of the solder can be improved by adding rare earth metals, e.g. lanthanum (La) and cerium (Ce) [4].

A higher number of elements in lead-free solder can solve the problem of the melting temperature as well. Namely, the solder materials of highest importance in practice, the SAC alloys (S = tin, A = silver, C = copper) have a higher melting point than the Sn-Pb solders. From the viewpoint of technology, this means that the currently used Printed Circuit Boards (PCBs) must be exchanged for higher temperature tolerant PCBs, which involves higher costs. Solder pastes from nano-sized alloy particles are a promising technique for decreasing the melting point of the solder [5].

Nanoparticles (NPs) are also adapted to improve the mechanical properties, as reinforcing materials. Nowadays, composite materials are widely used for improving the properties of materials. Based on this, we can assume that composites are able to fulfil an important role in soldering technology.

### 1. Classes of particles for composite solder materials

Nano- and micro-sized particles or fibres are applicable for the preparation of the composite solder. These reinforcing phases can be metals, oxide-, carbide- or nitride ceramics or non-metals, e.g. carbon nanotubes (CNTs). The reinforcing materials can be classified into the following groups according to their behaviour with the solder material [6, 7]:

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In Group I we can categorise the nano- and micro-sized solid phases whose particles may react with a component of the solder and can dissolve in the matrix during the melting or reflow to create an IMC on the solder/substrate interface. On this basis, the elements belonging here are Al, Fe, Zn, Ni, Ag, Cu and Co. These elements may be used as micro-sized particles. In this case, due to the larger size of the particles they cannot completely dissolve in the solder materials, and a “flower-like” IMC structure can form on the surface of these micro-sized particles. The properties of the micro-sized-particle reinforced composite solder tend to deteriorate because of the flower-like structure, which can cause cracks.

The solder material can be composed of nano-sized particles, namely the solder particles are dispersed in an organic medium. This solder material is the paste. Without oxide or any other reinforcing material in this paste it is not a composite solder.

In Group II the nano-sized intermetallic phases are categorised, e.g. Sn<sub>6</sub>Cu<sub>5</sub>, Cu<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>4</sub> and Ag<sub>3</sub>Sn. The equilibrium can be reached by using these particles and thus the reactivity between the solder and the substrate can be reduced. In this case the melted solder is not able to create a crater in the substrate in contrast with the solder without intermetallic nanoparticles.

The inert nano- and micro-particles belong to Group III, e.g. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and CNTs. These particles do not react with the solder material but they are suited for acting as the sites for the heterogeneous nucleation of β-tin or intermetallic phase, so the size of β-tin and IMC can be reduced significantly on the interface of the solder/substrate.

In the development of a composite solder, similarly to other metal matrix composites [8, 9]. It is necessary to consider that the surface of the reinforcing materials is not wetted perfectly by the melted alloys, which means the adhesion between solder and reinforcing phases is weak. The adhesion can be improved by a metallic coating on the surface of the reinforcing materials, e.g. nickel coating on the surface of CNTs [10].

2. Preparation of the composite solders

The metal matrix composites can be categorised according to the preparation of the reinforcing materials. Accordingly we can speak about ex-situ and in-situ composites [11].

2.1. Ex-situ composites

Inert reinforcing particles can be mixed or stirred with the melted solder material. In this casting method the melted solder should be prevented from oxidation by using an inert gas atmosphere [12].

Solder paste can be made with reactive reinforcing materials that can react with the solder or can dissolve in the alloy. In this case we can prepare solder paste from the particles of the components. In preparing the solder paste, the reactive particles can be dispersed with the solder powder in a special water or organic solvent soluble flux [12–14].

Bulk solder (strip or wire) can be prepared by a method to avoid chemical reaction between the solder and the reinforcing particles before the soldering. First, the reinforcing particles and the powder of the solder alloy are homogenously mixed in alcohol. After the
drying of this slurry, the desired solder strip or wire can be prepared by cold forming methods.

2.2. In-situ composites

Recently, the development of in-situ composites has been investigated by several research groups [12, 15–17]. The reinforcing materials are prepared by the reaction between the elements of the solder alloy, e.g. Cu$_5$Sn$_5$ phase from the reaction of Sn and Cu. The required elements of the solder are melted and kept at a given temperature for the formation of the desired IMC phase in the alloy, then the alloy is cooled down and hot rolled. In this way the IMC phases will be micro-sized and well dispersed [12, 15].

3. Application of metal nanoparticles

There are two main groups of metal nanoparticles according to their behaviour with the solder material. In the first group we can find the metallic particles that are dissolved in solders such as Ag or Cu. The non-soluble metal particles (e.g. Mo) belong to the other group.

The most commonly used nano- or micro-sized particles for the developing of the solders are from Cu [18], Ag [19], Al [20], Zn [21], Mo [22, 23], Co [24, 25], Ni [26] and Sb [27]. These particles have been used for the production of Sn-Ag based solder, e.g. Sn-3.5Ag, and different SAC alloys, as well as for Sn-Pd, Sn-Cu and Sn-Zn alloys [7].

3.1. Interfacial behaviour of the solders containing metal nano- and micro-particles

The wettability of the copper plate can be improved by copper, nickel, or silver nanoparticles containing lead-free solders [6]; similarly, the solders which contain these elements as alloys but not nanoparticles [28].

Mo nanoparticles in Sn-Ag-Cu solder remain stable during multiple reflow cycles at 250 °C and the Mo nanoparticles do not dissolve in the matrix [23]. The molybdenum nanoparticles affect the formation of the IMC phase on the solder/substrate interface. The addition of Mo NPs to solder causes a decrease in the thickness of the IMC layer on the interface.

The effect of the Mo NPs and the insoluble NPs was explained by Haseeb [23], based on a study by Kim and Tu (cited in [23]). There are two IMC layers on the solder/substrate interface in the SAC solder/Cu substrate system. There is a Cu$_5$Sn$_5$ IMC layer on the Cu side. The Cu$_5$Sn$_5$ layer is covered by an IMC layer of Cu$_3$Sn$_3$ scallops which is directly on the solder side. Fluid channels exist between the Cu$_5$Sn$_5$ scallops, and these channels are extended to the Cu$_3$Sn$_3$/Cu interface. The fluid channels allow the possibility of quick diffusion for the dissolved copper, which results in further reaction and the extra Cu creates a thicker IMC layer on the interface. In the composite solder the non-soluble NPs can block the fluid channels, because the NPs are sorbed on the surface of the IMC.

The visible contact angle of the solder is increased and the spreading rate is decreased by the addition of non-soluble NPs or fibres to the solder, as shown in Table 1. The viscosity of the solder is increased by adding non-soluble NPs [29]. The higher viscosity keeps the solder from the spreading that gives rise to the increasing of the contact angle [30]. The increased contact angle value, however, is in the $20^\circ \leq \Theta \leq 40^\circ$ range, which is the necessary contact angle range for soldering.
The metal NPs are important for preparing the composite solder, but the solder itself can be made using metal NPs. In this case, the solder NP are mixed with solder flux and/or other organic components [31]. Solder pastes prepared with metal NPs have a lower melting point than bulk solder with the same composition [5, 32–37]. These results show a good agreement with the theoretical model as well [35, 36].

The behaviour of the melting point of the SAC alloy as a function of particle size was investigated by Gao et al. [32]. In their work an SAC alloy with grain size between 15–60 nm was produced and its melting behaviour was investigated by calorimetry. The melting point of the alloy changed from 218 °C to below 190 °C, while the particle size changed from micron size to 10 nm [32]. This melting point is equivalent to the melting point of bulk Sn-Pb alloys, which is between 183 °C and 190 °C [38]. Nano-sized solder alloys, which have a higher melting point than bulk, are applicable for lower temperature soldering. In this way the lower temperature tolerant PCBs do not have to be changed to higher temperature tolerant PCBs.

### 3.2. Mechanical properties of solder prepared with metallic nanoparticles

In the development of a solder, there is high interest in its mechanical properties, because the solder bond used in equipment is liable to mechanical stress, such as vibrations, or shocks caused by being dropped. The mechanical properties of the metal NPs containing solder will be illustrated in the following examples. The first example is Sn-3.5Ag solder containing Co NPs (Sn-3.5Ag-CoNPs). The shear strength of Sn-3.5Ag-CoNPs compared to Sn-3.5Ag improves as a function of the amount of the CoNPs. About 0.1 w% Co NPs in the solder causes an improvement in shear strength by ~28%. The shear strength of the Sn-3.5Ag-Co NPs composite solder reaches its maximum value at 0.1 wt.% CoNPs and from ~1.0 w% CoNPs the shear strength begins to decrease significantly; at 2.0 w% CoNPs reaches the value of the matrix material [39].

The silver in Sn-Zn-AgNPs composite solder improves the mechanical properties as well. The shear strength of a Sn-Zn-AgNPs composite rises as function of the amount of AgNPs. The shear strength of the Sn-Zn alloy decreases with increasing reflow number. The shear strength of Sn-Zn-AgNPs composite solder is independent of the reflow number. The good mechanical properties are due to the formation of spherical-shaped AgZn3IMC phases that are small in diameter, which can agglomerate and create micrometer-sized AgZn3 islands in the solder [40].

The mechanical properties of Sn-3.5Ag solder can be improved by Ni and Mo nanoparticles. An increase in the amount of MoNPs causes higher hardness; moreover, the addition of Mo NPs and NiNPs can also improve the resistance against creep [41].

<table>
<thead>
<tr>
<th>Solder</th>
<th>Wetting angle(θ), °</th>
<th>Spreading rate, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-3.8Ag-0.7Cu</td>
<td>19.46 ± 4.34</td>
<td>82.48 ± 2.42</td>
</tr>
<tr>
<td>Sn-3.8Ag-0.7Cu-0.18-CoNPs</td>
<td>26.95 ± 1.02</td>
<td>74.12 ± 4.85</td>
</tr>
<tr>
<td>Sn-3.8Ag-0.7Cu-0.41-CoNPs</td>
<td>25.76 ± 1.47</td>
<td>73.40 ± 5.32</td>
</tr>
<tr>
<td>Sn-3.8Ag-0.7Cu-0.75-CoNPs</td>
<td>26.71 ± 1.17</td>
<td>60.86 ± 5.32</td>
</tr>
</tbody>
</table>

Table 1: Wetting angle and spreading rate of SAC on Cu substrate with various addition of Co NPs [29]
4. Application of oxide- and carbide ceramics and non-metallic materials

In the development of composite solders not only metal NPs are used; ceramic or non-metallic nano-sized phases can also be used as reinforcing phase. The non-metallic reinforcing particles can be composed of oxides, e.g. TiO₂ [42, 43, 44], Al₂O₃ [45, 46], ZrO₂ [47] or Fe-Ni-oxide [48]; carbides, such as the most commonly used SiC [49, 50]; borides, e.g. TiB₂ [30]; as well as nanostructured POSS (polyhedral oligomeric Silsesquioxane) [51] or CNTs and fibres [10, 52, 53]. These materials are applied in order to improve mechanical properties, e.g. hardness and tensile strength, as well as shear strength.

4.1. Wettability and interfacial properties of ceramic NP reinforced composite solder

The ceramics and non-metallic reinforcing phases can be classified into two groups. Inert materials (e.g. Al₂O₃, TiO₂) belong to the first group; these materials do not react with the components of the solder. Reactive particles, for example SnO₂ [6], belong to the second group. These particles can react or dissolve in the solder. Thus, for the two groups a different effect can be observed in the wetting properties.

The wettability and spreading of the Sn3.5Ag0.7Cu-MWCNT (multi-walled carbon nanotube) and Sn-3.5Ag-0.7Cu-TiB₂NPs composite solders were investigated by Nai et al. [30]. They determined that the contact angle decreases as a function of increasing the amount of TiB₂ NPs in the solder. The composite solder can reach the minimum contact angle at 2 vol% TiB₂ NPs content. The viscosity of the solder is increased by a higher amount of TiB₂ NPs, so the solder is not able to spread on the surface of the substrate, as seen also in Subsection 3.1 in connection with the CoNPs. This gives a higher contact angle.

The improvement of the wetting of the composite solder was observed with a small amount of other NPs, e.g. TiO₂ (minimum contact angle at 0.1 w% TiO₂ [54]), Y₂O₃ (minimum contact angle at 1 w% Y₂O₃ [55]) and Al₂O₃ (minimum contact angle at 0.5 w% Al₂O₃ [56]).

4.2. The mechanical properties of solder-ceramic NP composites

Ceramic NPs, similar to metal particles, improve the mechanical properties of the composite solders. Gain et al. [47] observed that 0.5 w% ZrO₂ NPs can significantly improve the shear strength compared to solder without NPs. In addition, the reflow number causes only a small decline in the shear strength if the solder consists of NPs compared to the solder without NPs. We can say from the data in Table 2 that the tensile strength of the composite solder is increased and its ductility is decreased by the addition of oxide NPs or CNTs.

### Table 2

<table>
<thead>
<tr>
<th>Solder</th>
<th>Reinforcing phase</th>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tensile strength, Rₚₙ, MPa</td>
</tr>
<tr>
<td>Sn3.0Ag0.5Cu</td>
<td>0.00 w%TiO₂</td>
<td>40.90</td>
</tr>
<tr>
<td></td>
<td>0.25 w%TiO₂</td>
<td>45.80</td>
</tr>
<tr>
<td></td>
<td>0.50 w%TiO₂</td>
<td>49.10</td>
</tr>
<tr>
<td></td>
<td>0.75 w%TiO₂</td>
<td>53.00</td>
</tr>
<tr>
<td></td>
<td>1.00 w%TiO₂</td>
<td>57.00</td>
</tr>
<tr>
<td></td>
<td>1.25 w%TiO₂</td>
<td>56.00</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th></th>
<th>Sn3.5Ag0.5Cu</th>
<th>Sn3.8Ag0.7Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 w% Al₂O₃</td>
<td>54.30</td>
<td>37.70</td>
</tr>
<tr>
<td>0.25 w% Al₂O₃</td>
<td>60.20</td>
<td>40.90</td>
</tr>
<tr>
<td>0.50 w% Al₂O₃</td>
<td>62.40</td>
<td>44.28</td>
</tr>
<tr>
<td>1.00 w% Al₂O₃</td>
<td>68.05</td>
<td>53.47</td>
</tr>
<tr>
<td>1.50 w% Al₂O₃</td>
<td>70.05</td>
<td>56.70</td>
</tr>
<tr>
<td>0.00 w% SWCNT*</td>
<td>33.30</td>
<td>26.60</td>
</tr>
<tr>
<td>0.01 w% SWCNT</td>
<td>32.70</td>
<td>23.28</td>
</tr>
<tr>
<td>0.08 w% SWCNT</td>
<td>27.32</td>
<td>24.36</td>
</tr>
<tr>
<td>0.10 w% SWCNT</td>
<td>26.57</td>
<td></td>
</tr>
<tr>
<td>0.80 w% SWCNT</td>
<td>23.28</td>
<td></td>
</tr>
<tr>
<td>1.00 w% SWCNT</td>
<td>24.36</td>
<td></td>
</tr>
</tbody>
</table>

*SWCNT: single-walled carbon nanotube

Summary

In accordance with European Union legislation lead and other critical alloying elements have to be removed and replaced by non-hazardous elements in the certain segments of the soldering technology. In the interest of achieving the mechanical and thermal properties of the tin-lead alloy, it is necessary to use two, three or even more alloying elements in the newly developed lead-freesolder.

Several lead-free solders have a higher melting point than the melting temperature of the Sn-Pb alloys. The higher soldering temperature required a change in PCB from lower temperature to higher temperature resistant PCBs. This industrial problem (the change of the PCB) can be solved by using a solder paste made from metal NPs. Solder pastes from nano-sized alloy particles have a lower melting point than the bulk solder with same composition, and their temperature is equivalent to the melting point of the Sn-Pb alloys.

In the development of the solder, its mechanical properties are important because equipment with solder bonding is liable to mechanical stress, such as vibration, or shock caused by falling. The mechanical properties, hardness, tensile strength and shear strength can be improved by adding non-reactive NPs, e.g. Al₂O₃. Moreover, the presence of NPs in solder may decrease the IMC layer thickness on the solder/substrate interface.

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