**Abstract:** An alloy suitable for use in tinning or the manufacture of heat exchangers, the alloy comprising: from 2 - 6 wt.% copper, from 0.08 - 1.5 wt.% bismuth, from 0 - 1.5 wt.% silver, from 0 - 0.02 wt.% phosphorus, from 0 - 0.02 wt.% germanium, from 0-0.15 wt% of indium, from 0-0.3 wt% of silicon, from 0-0.2 wt% of zirconium, one or both of from 0.02 - 0.2 wt.% nickel and/or from 0.01 - 0.2 wt.% cobalt, and the balance tin, together with unavoidable impurities.
Lead-free solder alloy

The present invention relates to an alloy and, in particular, a lead-free solder alloy. The alloy is particularly, though not exclusively, suitable for use in tinning of thin copper wires and the manufacture of copper and brass heat exchangers.

For environmental reasons, there is an increasing demand for lead-free replacements for lead-containing conventional alloys.

In many electronic applications, soldering takes place at a relatively low temperature, typically 235 to 260°C. Many lead-free solder alloys have been proposed for use in this temperature range.

For other applications, the soldering process may need to be conducted at a higher temperature. However, the use of a higher temperature can lead to problems resulting from the increased rate of dissolution of the substrate into the molten solder. For example, in the manufacture of heat exchangers, copper or copper-alloy (e.g., brass) tubes are coated with solder in preparation for the construction of the radiator core. The coating process involves applying flux to the outside of the tube, and then passing the tube through a tank of molten solder, so that the outside surface is wetted by the solder. As a consequence, a thin film, typically 5 to 8 microns, is left on the tube as it exits the tank. In order to provide sufficient heat transfer in a reasonably short contact time, a solder bath temperature of from 330 to 350°C is commonly used. The relatively high
temperature means that the solder bath will absorb copper (dissolved from the tubes) more quickly than is the case for a low temperature process. This results in a gradual increase in the copper content of the bath. Although careful management of the composition of the bath, and the use of different top-up alloys can help, the problem is at least a nuisance to the operator.

A second high-temperature application is commonly referred to as "lead dipping". In this process the objective is to coat the end of a copper wire with a few microns of solder alloy. This coating (tinning) enhances the solderability of that section of wire, which facilitates joining it to another surface in a subsequent soldering operation. The surface of the bare copper wire may be coated with an organic compound to provide corrosion protection. This coating must be removed before the copper wire can be tinned. If the lead "dipping" operation is performed at a relatively high temperature, for example $350 \, ^\circ C$ or above, then the organic coating can be burned off, and the tinning can be accomplished in a single operation. However, if conventional lead-free solder alloys are used in such a "tinning" or "dipping" operation, dissolution of the copper wire can occur owing to the aggressive nature of the conventional alloys at the temperatures involved. Since the wire will often be of very fine gauge, this loss of material can be a problem.

There are a number of requirements for a solder alloy to be suitable for use in the above-described high temperature applications. First, they must be able to wet the substrate quickly. Second, they must be of suitable
composition so that they can be held in a molten bath for extended periods without excessive dross formation. Third, the solder joints formed from the alloys must be sufficiently strong for the conditions of service. Fourth, where the solder is in the form of a coating, the alloy must be compatible with the soldering operation and the soldering material that will ultimately be applied.

The present invention aims to address at least some of the problems associated with the prior art and to provide an improved solder alloy. Accordingly, the present invention provides an alloy suitable for use in tinning or the manufacture of copper and brass heat exchangers, the alloy comprising:

- from 2 - 6 wt.% copper,
- from 0.08 - 1.5 wt.% bismuth,
- from 0 - 1.5 wt.% silver,
- from 0 - 0.02 wt.% phosphorus,
- from 0 - 0.02 wt.% germanium,
- from 0 - 0.15 wt% of indium,
- from 0 - 0.3 wt% of silicon,
- from 0 - 0.2 wt% of zirconium,
- one or both of
  - from 0.02 - 0.2 wt.% nickel and/or
  - from 0.01 - 0.2 wt.% cobalt,
- and the balance tin, together with unavoidable impurities.
The present invention will now be further described. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

Copper provides strength to the resulting tin solder, and in general terms its presence reduces the rate of copper dissolution from the substrate. Higher copper values slow the rate of copper dissolution, but also increase the liquidus temperature. For these reasons, the inventors have found that the optimum copper content, in conjunction with the other alloying elements, to achieve the desired balance is from 2 - 6 wt.%, more preferably from 2 - 4.5 wt.%, still more preferably from 2 - 4 wt.%. The lower limit in respect of the Cu may preferably be at least 2.1 wt.%, still more preferably at least 2.3 wt.%, still more preferably at least 2.5 wt.%.

Bismuth strengthens the alloy and is also believed to help in the wetting of the solder to the surface. It is also possible that bismuth, in conjunction with other elements present in the alloy, reduces the dissolution rate of copper. For these reasons, the inventors have found that the bismuth content, in conjunction with the other alloying elements, should be from 0.08 - 1.5 wt.%, preferably from 0.08 - 1 wt.%, more preferably from 0.08 - 0.8 wt.%, still more preferably from 0.08 - 0.3 wt.%. If the lower limit is less than 0.08 wt.%, then it has been found that the
benefits derived from presence of bismuth, notably the mechanical and soldering properties for the applications in question, may not be sufficient. For this reason, the lower limit in respect of the bismuth is preferably 0.1 wt.%, more preferably 0.12 wt.%, still more preferably 0.15 wt.%. However, the content of bismuth in the alloy preferably does not exceed 1 wt.%. This is because it has been found that high bismuth levels result in a brittle alloy and, furthermore, reduce the solidus of the alloy. For these reasons, the content of bismuth in the alloy preferably does not exceed 0.8 wt.%, more preferably it does not exceed 0.5 wt.%, still more preferably it does not exceed 0.3 wt.%.

The presence of nickel and/or cobalt in the alloy has been found to strengthen the alloy owing to the formation of intermetallic compounds. Nickel and cobalt also reduce the rate of copper dissolution to more manageable levels. For these reasons, the alloy comprises, in conjunction with the other alloying elements, from 0.02 - 0.2 wt.% nickel and/or from 0.01 - 0.2 wt.% cobalt. More preferably, if present, the alloy comprises from 0.02 - 0.1 wt.% nickel. Similarly, if present, the alloy preferably comprises from 0.01 - 0.1 wt.% cobalt.

The presence of silver, an optional alloying element, in the alloy has been found to promote wetting and to improve the strength of the alloy. At low levels, the inventors have found that the silver does not have any significant effect on the dissolution rate of copper into the solder. In other words, the inventors have found that improved solder wetting and improved alloy strength, which can be derived from silver, can be achieved at low levels.
The use of low levels of silver has also been found to be advantageous in that higher levels of silver result in an increased copper dissolution rate and excessive numbers of large silver intermetallic crystals. For these reasons, the alloy preferably contains no more than 1.5 wt.% silver, for example from 0.1 to 1.5 wt.%. More preferably, the alloy contains no more than 1 wt.% silver, still more preferably no more than 0.5 wt.% silver, still more preferably no more than 0.3 wt.% silver. A low silver content (for example ≤ 1 wt.%, more preferably ≤ 0.5 wt.%) has also been found to be beneficial because, in conjunction with the other alloying elements, it provides reduced alloy stiffness. A preferred range is therefore 0.1 to 0.5 wt.%, more preferably 0.1 to 0.3 wt.%. 

The presence of phosphorus and/or germanium in the alloy is believed to reduce the volume of dross formed on the top of an open tank of solder. Accordingly, if present, the alloy preferably comprises up to 0.01 wt.% phosphorous. Similarly, if present, the alloy preferably comprises up to 0.01 wt.% germanium.

Indium, if present, has been found to assist the wetting of the solder to copper substrates. Zirconium and/or silicon, if present, have been found to beneficially affect the rate of intermetallic growth at the interface in subsequent ageing of the solder joint.

The alloys according to the present invention are lead-free or essentially lead-free. The alloys offer environmental advantages over conventional lead-containing solder alloys.
It will be appreciated that the alloys according to the present invention may contain unavoidable impurities, although, in total, these are unlikely to exceed 1 wt.% of the composition. Preferably, the alloys contain unavoidable impurities in an amount of not more than 0.5 wt.% of the composition, more preferably not more than 0.3 wt.% of the composition.

The alloys according to the present invention will typically be supplied as a bar, stick or ingot, optionally together with a flux. The alloys may also be provided in the form of a wire, for example a cored wire, which -- incorporates a flux, a sphere, or other preform typically though not necessarily made by cutting or stamping from a strip or solder. These may be alloy only or coated with a suitable flux as required by the soldering process. The alloys may also be supplied as-- a powder, or as a powder blended with a flux to produce a solder paste.

The alloys according to the present invention may be used in molten solder baths. Accordingly, the present invention further provides a solder bath or tank for soldering or coating or tinning of a substrate material, wherein the solder bath contains an alloy as herein described in the molten state.

The alloys will typically comprise at least 89.9 wt.% tin, preferably from 90 to 97.9 wt.% tin, more preferably from 94 to 97.5 wt.% tin, still more preferably 95 to 97.5 wt.% tin. Accordingly, the present invention further
provides an alloy for use in tinning or the manufacture of heat exchangers, the alloy comprising:

- from 90 - 97.9 wt% tin,
- from 2 - 6 wt.% copper,
- from 0.08 - 1.5 wt.% bismuth,
- from 0 - 1.5 wt.% silver,
- from 0 - 0.02 wt.% phosphorus,
- from 0 - 0.02 wt.% germanium,
- from 0 - 0.15 wt% of indium,
- from 0 - 0.3 wt% of silicon,
- from 0 - 0.2 wt% of zirconium,

one or both of from 0.02 - 0.2 wt.% nickel and/or from 0.01 - 0.2 wt.% cobalt,

and unavoidable impurities.

The alloys according to the present invention may consist essentially of the recited elements. It will therefore be appreciated that in addition to those elements which are mandatory (i.e. Sn, Cu, Bi and at least one of Ni, and Co) other non-specified elements may be present in the composition provided that the essential characteristics of the composition are not materially affected by their presence. Accordingly, the present invention further provides an alloy for use in tinning or the manufacture of heat exchangers, the alloy consisting essentially of:

- from 90 - 97.9 wt% tin,
- from 2 - 6 wt.% copper,
from 0.08 - 1.5 wt.% bismuth,

from 0 - 1.5 wt.% silver,
from 0 - 0.02 wt.% phosphorus,
from 0 - 0.02 wt.% germanium,
from 0 - 0.15 wt% of indium,
from 0 - 0.3 wt% of silicon,
from 0 - 0.2 wt% of zirconium,

one or both of from 0.02 - 0.2 wt.% nickel and/or
from 0.01 - 0.2 wt.% cobalt,

and unavoidable impurities.

The present invention also provides a soldered joint or coating comprising an alloy as herein described.

The alloys according to the present invention are particularly well suited to applications involving tinning (or dipping) of thin copper wires and the manufacture of copper and copper-alloy (eg brass) heat exchangers.

The present invention will now be described further with reference to the following non-limiting examples.

Examples

Example 1

Suitable quantities of the alloys Sn - 5 wt.% Cu, Sn - 52 wt.% Bi and Sn - 0.3 wt.% Ni were prepared by dissolving the elements into molten tin. Appropriate weights of the
resulting master alloys were then melted together to form an alloy whose composition was shown by analysis to be:

\[
\begin{align*}
\text{Cu} & \quad 2.8 \text{ wt.\%} \\
\text{Bi} & \quad 0.12 \text{ wt.\%} \\
\text{Ni} & \quad 0.06 \text{ wt.\%} \\
\text{Balance Sn}
\end{align*}
\]

Copper wires were dipped into a flux (AlphaFry RF800) and then immersed into the solder composition at 350°C. The wires were thereby coated with a thin protective layer of solder. The solder prevents oxidation of the copper wires so that they can then be more readily soldered.

Example 2

Using pre-prepared master alloys, an alloy of the following composition was prepared:

\[
\begin{align*}
\text{Cu} & \quad 3.0 \text{ wt.\%} \\
\text{Ag} & \quad 0.25 \text{ wt.\%} \\
\text{Bi} & \quad 0.25 \text{ wt.\%} \\
\text{Ni} & \quad 0.05 \text{ wt.\%} \\
\text{P} & \quad 0.005 \text{ wt.\%} \\
\text{Balance Sn}
\end{align*}
\]

The alloy was melted in a tank and maintained at a temperature of 335°C. A brass strip was fluxed, pre-warmed and then run through the tank so that it was immersed in the molten solder for approximately three seconds. A uniform coating of solder was produced on the surfaces of the strip. Optionally excess solder may be removed using hot air jets.
at the surface, or by means of a heated die or scraper though which the coated strip is passed.

Example 3

An alloy of the following composition was prepared using the techniques outlined in the example above:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.1 wt.%</td>
</tr>
<tr>
<td>Ag</td>
<td>0.4 wt.%</td>
</tr>
<tr>
<td>Bi</td>
<td>0.12 wt.%</td>
</tr>
<tr>
<td>Co</td>
<td>0.035 wt.%</td>
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<tr>
<td>Ni</td>
<td>0.04 wt.%</td>
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<tr>
<td>Balance</td>
<td>Sn-</td>
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</table>

The alloy was cast into a billet, and then extruded and drawn into wire. Slugs of wire were then cut and pre-melted into the base of a fuse cap. The cap containing the solder was then used in the manufacture of a safety fuse. In this example, the particular advantage of the low dissolution rate of the fuse wire alloy into the molten solder is a benefit.
CLAIMS:

1. An alloy suitable for use in tinning or the manufacture of heat exchangers, the alloy comprising:

   from 2 - 6 wt.% copper,
   from 0.08 - 1.5 wt.% bismuth,

   from 0 - 1.5 wt.% silver,
   from 0 - 0.02 wt.% phosphorus,
   from 0 - 0.02 wt.% germanium,
   from 0 - 0.15 wt% of indium,
   from 0 - 0.3 wt% of silicon,
   from -0.2 wt% of zirconium,

   one or both of from 0.02 - 0.2 wt.% nickel and/or from 0.01 - 0.2 wt.% cobalt,

   and the balance tin, together with unavoidable impurities.

2. An alloy as claimed in claim 1, comprising from 2 - 4.5 wt.% copper, preferably from 2 - 4 wt.% copper.

3. An alloy as claimed in claim 1 or claim 2, comprising from 0.08 - 0.8 wt.% bismuth, preferably from 0.08 - 0.3 wt.% bismuth.

4. An alloy as claimed in any one of the preceding claims, comprising from 0.02 - 0.1 wt. % nickel.
5. An alloy as claimed in any one of the preceding claims, comprising from 0.01 - 0.1 wt.% cobalt.

6. An alloy as claimed in any one of the preceding claims, comprising up to 0.5 wt.% silver, preferably up to 0.3 wt.% silver.

7. An alloy as claimed in any one of the preceding claims, comprising up to 0.01 wt.% phosphorus.

8. An alloy as claimed in any one of the preceding claims, comprising up to 0.01 wt.% germanium.

9. An alloy as claimed in any one of the preceding claims in the form of a bar, a stick, an ingot, optionally together with a flux, a solid or flux-cored wire, a foil or strip, or a powder or paste (powder plus flux blend), or solder spheres or other pre-formed solder pieces.

10. A solder bath or tank for soldering or coating or tinning of a substrate material, wherein the solder bath contains an alloy as defined in any one of claims 1 to 9 in the molten state.

11. A soldered joint or coating comprising an alloy as defined in any one of claims 1 to 9.
**A. CLASSIFICATION OF SUBJECT MATTER**

INV. B23K35/26 C22C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
B23K C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search: 5 February 2007

Date of mailing of the international search report: 15/02/2007

Name and mailing address of the ISA:
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Fax (+31-70) 340-3016

Authorized officer:
Vl assi, Eleni
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Form PCT/ISA/21O (patent family annex) (April 2005)