Machinable copper-based alloy and production method

Technical field

The present invention concerns an alloy based on copper, nickel, tin, lead and its production method. In particular, though not exclusively, the present invention concerns an alloy based on copper, nickel, tin, lead easily machined by turning, slicing or milling.

State of the art

Alloys based on copper, nickel and tin are known and widely used. They offer excellent mechanical properties and exhibit a strong hardening during strain-hardening. Their mechanical properties are further improved by the known heat-aging treatment such as spinodal decomposition. For an alloy containing, by weight, 15% of nickel and 8% of tin (standard alloy ASTM C72900), the mechanical resistance can reach 1500 MPa.

Another favorable property of the Cu-Ni-S alloys is that they offer good tribological properties, comparable to those of bronzes, while exhibiting superior mechanical properties.

Another advantage of these materials is their excellent formability, combined with favorable elastic properties. Moreover, these alloys offer a good resistance against corrosion and an excellent resistance to the constraints' heat relaxation. For this reason, the Cu-Ni-Sn springs do not lose their compression force with age, even under vibrations and strong heat stresses.

These favorable properties, combined with good heat and electricity conductivity, mean that these materials are widely used for making highly reliable connectors for telecommunications and the car industry. These alloys are also used in several switches and electrical or

electromechanical devices or as supports of electronic components or for making bearing friction surfaces subjected to high charges.

The Cu-Be alloys can be machined fairly well and can contend with and even outperform the mechanical properties of Cu-Ni-Sn alloys. The machinability index of the Cu-Be alloys can reach 50-60% relatively to standard ASTM C36000 brass. Their cost is however high and their production, use and recycling are particularly constraining because of the beryllium's high toxicity. The resistance to the constraints' heat relaxation of these materials is lower than that of the Cu-Ni-Sn for temperatures above 150-175°C.

One inconvenience of the Cu-Ni-Sn alloys is however that they are poorly suited to processes such as milling, turning or slicing or to any other known process. A further inconvenience of these alloys is their strong segregation during casting.

It is thus an aim of the present invention to propose an alloy associating the favorable mechanical characteristics of alloys based on copper, nickel and tin with a good workability.

It is another aim of the present invention to propose a method for producing a machinable product on the basis of Cu-Ni-Sn free from the inconveniences of the prior art.

It is another aim of the present invention to propose a machinable alloy combining high elasticity and mechanical resistance characteristics but free from beryllium or toxic elements.

A further aim of the present invention is to propose a method for producing a machinable product on the basis of Cu-Ni-Sn allowing the problems relative to segregation to be solved.

These aims are achieved by the product and the method that are the object of the independent claims of corresponding category and

notably by a machinable product composed of an alloy comprising between 1% and 20% by weight of Ni, between 1% and 20% by weight of Sn, between 0.1% and 4% of Pb, the remainder being constituted essentially of Cu, having undergone a heat homogenizing treatment comprising a step of heating said alloy followed by a step of cooling at a speed sufficiently slow to prevent fissuring.

Detailed description of the invention

The present invention concerns alloys on the basis of copper, nickel, tin and lead obtained by a continuous or semi-continuous casting method, a static billet casting or casting by sprayforming. The copper-nickel-tin alloys have a long solidification interval leading to a considerable segregation during casting. Of the four aforementioned processes, casting by sprayforming, also known by the name "Osprey" method, and described for example in patent EP0225732 makes it a possible to obtain an almost homogenous microstructure presenting a minimal degree of segregation. In this process, a metal billet is obtained by continuous depositing of atomized droplets. The segregation can take place only on the scale of the atomized droplets. The diffusion distances required for diminishing the segregation are thus shortened. In the case of continuous or semi-continuous casting, the segregation is stronger than with the sprayforming process, but it remains sufficiently reduced to avoid an excessive fragility of the alloy. The static billet casting leads to a strong segregation that can be eliminated only by a prolonged heat processing.

Lead being essentially insoluble in the other metals of the alloy, the product obtained will comprise lead particles dispersed in a Cu-Ni-Sn matrix. During the machining operations, the lead has a lubricating effect and facilitates the fragmentation of the slivers.

The quantity of lead introduced in the alloy depends on the degree of machinability that one strives to achieve. Generally, a quantity of lead up to several percents by weight can be introduced without the alloy's mechanical properties at normal temperature being modified. However,

above the lead melting point (327 °C), the liquid lead strongly weakens the alloy. Alloys containing lead are thus difficult to make, on the one hand because they have a very strongly pronounced tendency towards fissuring and, on the other hand, because they can exhibit a two-phased crystallographic structure containing an undesirable weakening phase.

The method of the present invention makes it possible to produce a machinable Cu-Ni-Sn-Pb product containing up to several percents by weight of lead, without it fissuring during fabrication, and having excellent mechanical properties. The ratio of lead can vary between 0.1% and 4% by weight, preferably between 0.2% and 3% by weight, even more preferably between 0.5% and 1.5% by weight.

After smelting in the foundry, the production methods can be decomposed in successive slugs: for the first slug, two cases must be considered according to whether the product is manufactured by continuous casting at small diameter or by static billet casting, sprayforming, semi-continuous or continuous casting at large diameter.

The products of the invention are characterized by their excellent machinability, which is greater than that of Cu-Be alloys. The machinability index of the inventive alloys exceeds 80% relatively to standard ASTM C36000 brass and can even reach 90%.

First slug:

Alloys obtained by continuous small-diameter thread casting, e.g. of 25mm or less, undergo a heat homogenizing treatment or a step of cold deformation by hammering followed by a homogenizing and recrystallization treatment. The temperature of the heat treatment must be within the range where the alloy is one-phased. Cooling after the heat treatment must occur at a speed sufficiently slow to prevent fissuring of the alloy due to internal constraints generated by the temperature differences during cooling, and sufficiently fast to limit the formation of a two-phased structure. If the speed is too slow, a considerable quantity of second phase

can appear. This second phase is very fragile and greatly reduces the alloy's deformability. The critical cooling speed required to avoid the formation of too large a quantity of second phase will depend on the alloy's chemistry and is greater for a higher quantity of nickel and tin.

Moreover, during cooling, transitory internal constraints are generated within the alloy. They are linked to temperature differences between the surface and the center of the product. If these constraints exceed the alloy's resistance, the latter will fissure and is no longer usable. Internal constraints due to cooling are all the higher the more the product's diameter is large. The critical cooling speeds to avoid fissuring thus depend on the product's diameter. This problem is even more acute with Cu-Ni-Sn-Pb alloys since above its melting temperature of 327°C, lead strongly weakens the alloy.

In the method of the present invention, cooling after heat treatment occurs at a predetermined speed taking into account the alloy's chemistry and the transversal dimension, or diameter, of the product. The cooling speed must be at the same time sufficiently slow to prevent fissuring and sufficiently great to prevent too large a quantity of fragilizing phase to form.

During manufacture of a large-diameter product, the internal constraints due to the temperature differences are greater than in a small-dimension product, and the cooling speed must consequently be limited. At the same time, strong proportions of Ni and Sn promote the formation of a fragilizing phase and require a faster cooling.

Alloys obtained by sprayforming, static billet casting or semi-continuous casting undergo a hot extrusion treatment. This is also the case for continuous casting if the product is of large diameter. Cooling during extrusion must be sufficiently slow to prevent fissuring and sufficiently fast to limit the formation of a fragilizing second phase. Alternatively, if cooling during extrusion is too slow, heat homogenizing and recrystallization

treatments as explained here above for the case of small-diameter continuous-casting products must follow extrusion.

Once the first slug has been made, the final machinable product must be either obtained directly by one or several cold deformation operations, e.g. by rolling, wire-drawing, stretch-forming or any other cold deformation process, or obtained by one or several successive slugs.

Successive slugs:

From the first slug, the following slugs are obtained by one or several cold deformation operations followed by a heat recrystallization treatment. The temperature of the recrystallization treatment must be within the range where the alloy is one-phased. Cooling after the heat treatment must have a speed sufficiently slow to prevent fissuring but always sufficiently fast to limit the formation of a two-phased structure. Through successive slugs, the size of the product is reduced. From the last slug, the final product is obtained by one or several cold deformation operations.

The mechanical properties of the alloy obtained can be subsequently increased by a spinodal decomposition heat treatment. This treatment can take place before the final machining or after the latter.

Hereafter, examples of methods and of machinable products according to the present invention will be presented. In the following examples, the cooling temperatures refer to the center of the product.

Example 1

The chemical composition of the alloy in this example is given by table 1:

Table 1

Component	Proportion (by weight)
Cu	remainder
Ni	7.5%
Sn	5%
Pb	1%
Mn	0.1%-1%
other	<0.5%

Manganese is introduced in the composition as deoxidizer. It is however possible to use instead other elements or devices preventing the alloy from oxidizing.

This alloy can be cast according to the different methods mentioned further above. In this example, this alloy is obtained by continuous billet casting with a diameter of 180mm.

First slug: the billets are extruded for example to a diameter of 18mm. At the exit of the extrusion die, the alloy is cooled by a stream of compressed air allowing a cooling speed of 50°C/min to 300°C/min to be achieved, as measured at the center of the alloy. This speed is sufficiently slow to avoid fissuring and sufficiently fast to limit the formation of a fragilizing second phase. Cooling by water spray can also be used, possibly allowing cooling speeds of 300°C/min to 1000°C/min to be achieved without fissuring of the material. Other means for reaching a suitable cooling speed can also be used. If cooling at the exit of the extrusion die is not sufficiently fast, a too great a proportion of second phase can form, the alloy will have to undergo a homogenization treatment with the same characteristics for the cooling speed at a temperature within the range where the alloy is one-phased, i.e. between 690°C and 920°C for the composition of table 1.

Second slug: the material of the first slug at a diameter of 18mm is rolled to a diameter of 13mm then annealed in a through-type furnace or removable cover furnace. For the alloy with the chemical composition of example 1, the annealing temperature must be comprised between 690°C and 920°C. A cooling speed on the order of 10°C/min is sufficient to limit the formation of second phase for this composition and this diameter of

13mm. Furthermore, water spray cooling at speed of 300°C/min to 3000°C/min allows fissuring to be prevented and the formation of a fragilizing second phase to be limited.

Finishing: the material of the second slug is wire-drawn or stretch-formed to a diameter of 8mm to obtain a machinable product. A spinodal decomposition treatment is finally performed on the machinable product or on the machined pieces to obtain optimal mechanical properties.

Example 2

The chemical composition of the alloy in this example is given by table 2:

Table 2

Component	Proportion (by weight)
Cu	remainder
Ni	9%
Sn	6%
Pb	1%
Mn	0.1%-1%
Impurities	<0.5%

In this example, this alloy is obtained by continuous thread casting with a diameter of 18mm.

First slug: the thread undergoes a homogenization treatment in a through-type furnace at a temperature between 700°C and 920°C, corresponding to the one-phase range of the chemical composition of example 2. A cooling speed between 100°C/min and 1000°C/min allows fissuring to be prevented and the proportion of fragilizing second phase to be limited. Such cooling speeds can for example be achieved by using compressed air, water spray or a gas/water exchanging cooler.

Second slug: the material of the first slug at a diameter of 18mm is rolled, wire-drawn or stretch-formed to a diameter of 13mm then annealed in a through-type furnace at a temperature comprised between 700°C and 920°C. With a diameter of 13mm and the chemical composition

of table 2, a cooling speed between 100°C/min to 3000°C/min allows the formation of a second phase to be limited while avoiding fissuring.

Third slug: the material of the second slug at a diameter of 13mm is rolled, wire-drawn or stretch-formed to a diameter of 10mm then annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C. With a diameter of 10mm and the chemical composition of table 2, a cooling speed between 100°C/min to 15000°C/min allows the formation of a second phase to be limited without any fissuring being created.

Fourth slug: the material of the third slug at a diameter of 10mm is rolled, wire-drawn or stretch-formed to a diameter of 7mm then annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C. With a diameter of 7mm and the chemical composition of table 2, a cooling speed between 100°C/min to 20000°C/min allows the formation of a fragilizing second phase to be limited without any fissuring being created.

Fifth slug: the material of the fourth slug at a diameter of 7mm is rolled, wire-drawn or stretch-formed to a diameter of 5mm then annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C. With a diameter of 5mm and the chemical composition of table 2, a cooling speed between 100°C/min to 30000°C/min allows the formation of a fragilizing second phase to be limited without any fissuring being created. A cooling speed on the order of 15000°C/min can be achieved by tempering in appropriate fluids.

Sixth slug: the material of the fifth slug at a diameter of 5mm is rolled, wire-drawn or stretch-formed to a diameter of 3mm, annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C, then cooled at a cooling speed comprised between 100°C/min to 40000°C/min.

Seventh slug: the material of the sixth slug at a diameter of 3mm is rolled, wire-drawn or stretch-formed to a diameter of 2mm, annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C, then cooled at a cooling speed comprised between 100°C/min to 40000°C/min.

Eighth slug: the material of the seventh slug at a diameter of 2mm is rolled, wire-drawn or stretch-formed to a diameter of 1,60mm, annealed in a through-type furnace or tempering furnace at a temperature comprised between 700°C and 920°C, and then cooled at a cooling speed comprised between 100°C/min to 50000°C/min.

Finishing: the material of the eighth slug is rolled, wire-drawn or stretch-formed to a diameter of 1mm to obtain a machinable product. A spinodal decomposition treatment is finally performed on the machinable product or on the machined pieces to obtain optimal mechanical properties.

The "ASTM test method for machinability" test proposes a method for determining the machinability index relatively to standard CuZn39Pb3, or C36000 brass. The machinability index of the alloy according to this aspect of the invention is better by 80%.

Example 3

The chemical composition of the alloy in this example is the same as that of the second example given by table 2. In this example, the alloy is obtained by continuous casting at a diameter of 25mm.

First slug: the thread cast at a diameter of 25mm is hammered to a diameter of 16mm. The hammering allows the material to deform with a considerable reduction rate without prior heat homogenizing treatment. With this method, a high remainder ratio of fragilizing second phase can be tolerated at this stage. The second phase can reach a volume ratio on the order of 50%.

After hammering, the thread at a diameter of 16mm undergoes a homogenizing and recrystallization treatment in a through-type furnace. The temperature of the heat treatment must be comprised between 700°C and 920°C. The following cooling will take place at a speed comprised between 100°C/min and 3000°C/min. These cooling speeds make it possible to prevent fissuring and to limit the ratio of second phase for a product of this diameter and of this composition. Such speeds can be obtained by using compressed air, water spray or gas/water exchangers.

Finishing: the material of the first slug is wire-drawn or stretch-formed to a diameter of 10mm to obtain a machinable product. A spinodal decomposition treatment is finally performed on the machinable product or on the machined pieces to obtain optimal mechanical properties.

Example 4

The chemical composition of the alloy in this example is given by table 3:

Table 3

Component	Proportion (by weight)
Cu	remainder
Ni	15%
Sn	8%
Pb	1%
Mn	0.1%-1%
Impurities	<0.5%

This alloy can be cast according to the different methods mentioned here above. In this example, this alloy is obtained by sprayforming billets whose diameter is 240mm.

First slug: the billets are extruded for example to a diameter of 20mm. If the billets' dimensional irregularities are too great, a turning step can be necessary before extrusion. At the exit of the extrusion die, the alloy is cooled by water spray allowing a cooling speed of 300°C/min to 3000°C/min to be achieved, as measured at the center of the alloy. This

speed is sufficiently slow to avoid fissuring and sufficiently fast to limit the formation of a fragilizing second phase. If cooling at the exit of the extrusion die is not sufficiently fast, a too great a proportion of second phase can form. The alloy will then have to undergo a homogenization treatment with the same characteristics for the cooling speed at a temperature within the range where the alloy is one-phased, i.e. between 780°C and 920°C for the composition of table 3.

Second slug: the material of the first slug at a diameter of 20mm is hammered to a diameter of 11mm then annealed in a through-type furnace. For the alloy with the chemical composition of example 3, the annealing temperature must be comprised between 780°C and 920°C. With a diameter of 11mm and the chemical composition of table 3, a cooling speed comprised between 300°C/min and 15000°C/min allows the presence of second phase to be limited while avoiding fissuring. Use of hammering allows considerable strain-hardening rates to be achieved, even with a fragile material. With this method, the remainder rate of fragilizing second phase can be higher than with rolling, wire-drawing or stretch-forming methods. It can reach values on the order of 50% by volume.

Third slug: the material of the second slug at a diameter of 11mm is hammered to a diameter of 6,5mm then annealed in a through-type furnace or tempering furnace at a temperature comprised between 780°C and 920°C. With a diameter of 6,5mm the alloy of table 3 allows cooling speeds between 300°C/min to 20000°C/min without any fissuring. These speeds allow the ratio of fragilizing second phase to be limited.

Finishing: the material of the third slug is wire-drawn or stretch-formed to a diameter of 4mm to obtain a machinable product. A spinodal decomposition treatment is finally performed on the machinable product or on the machined pieces to obtain optimal mechanical properties.

Cooling test

Samples of the inventive alloy have been subjected to test of fast cooling to determine the occurrence of fissuring. The chemical composition of the alloy in this test is given by table 2.

The samples were subjected to a heat treatment at a temperature of 800°C and then cooled quickly by immersion in a tempering fluid (EXXON XD90) and in water.

For each cooling, the cooling speed, in °C/min, was measured with a thermocouple at the center of the sample. The presence of fissuring was verified by a traction test.

Table 5

diameter/mm	speed XD90	traction test	speed water	traction test
4	24000	O	63000	×
6	16000	O	48500	×
8	12000	O	33000	×
10.8	8350	O	-	×
13	6500	O/×	23500	×

(O = success / × = failure)

The test permits to observe that the diameters up to about 10mm can tolerate a cooling in a tempering fluid. Water tempering, on the other hand, always leads to a fissuring of the sample, and this up to a minimal diameter of 4mm.

For small-dimension products of Cu-Ni-Sn-Pb, cooling speeds greater than 24000°C/min can be used. In this case, water tempering can be efficient if the product's size is sufficiently small to limit the transitory internal constraints and thus prevent fissuring from forming.

The machinable products of the examples 1, 2, 3 and 4 can each be made by the methods of the examples 1, 2, 3 and 4 provided that the

cooling speeds and the heat treatment temperatures are adapted to the chemical compositions and to the dimensions. In each of the presented examples, the number of slugs can vary according to the size of the finished product.

Part of the copper of the alloys of the present invention can be replaced by other elements, for example Fe, Zn or Mn, at a ratio for example up to 10%.

Other elements such as Nb, Cr, Mg, Zr and Al can also be present, at a ratio up to several percents. These elements have among others the effect of improving the spinodal hardening.

Claims

1. Production method of a metallic product composed of an alloy comprising between 1% and 20% by weight of Ni, between 1% and 20% by weight of Sn, between 0.2% and 2% of Pb, the remainder being constituted essentially of Cu, the method comprising:

a heat treatment comprising a step of heating and homogenizing said alloy,

determining a cooling speed sufficiently slow to prevent fissuring and sufficiently high to limit the formation of a two-phased structure,

followed by a cooling step at the determined speed.

2. Method according to claim 1, wherein said heat treatment is followed by a step of cold deformation by rolling, wire-drawing, stretch-forming or hammering.

3. Method according to claim 1, wherein said heat treatment is performed in a through-type furnace.

4. Method according to claim 1, comprising an initial step of continuous casting followed by a hammering step or an initial step of static billet casting or a step of sprayforming billet casting, or a step of semi-continuous billet casting, followed by an extrusion step.

5. Method according to claim 1, wherein said heat treatment takes places at a temperature comprised between 690°C and 920°C.

6. Method according to claim 1, wherein the transversal dimension of said metallic product during said heat treatment is comprised between 1mm and 100mm.

7. Method according to claim 1, wherein said cooling step of said heat treatment has a cooling speed comprised between 10°C/min and

24000°C/min or between 10°C/min and 4000°C/min or between 100°C/min and 1500°C/min.

8. Method according to claim 1, wherein said cooling step of said heat treatment has a cooling speed comprised between 100°C/min and 1000°C/min.

9. Method according to claim 1, comprising a step of wire-drawing or stretch-forming or hammering or rolling.

10. Method according to claim 1, comprising a step of spinodal hardening.

11. Method according to claim 1, wherein said alloy comprises between 6% and 8% of Ni, between 4% and 6% of Sn and between 0.5% and 2% of Pb.

12. Method according to claim 1, wherein said alloy comprises between 8% and 10% of Ni, between 5% and 7% of Sn and between 0.5% and 2% of Pb.

13. Method according to claim 1, wherein said alloy comprises between 14% and 16% of Ni, between 7% and 9% of Sn and between 0.5% and 2% of Pb.

14. Product from the method of claim 1.