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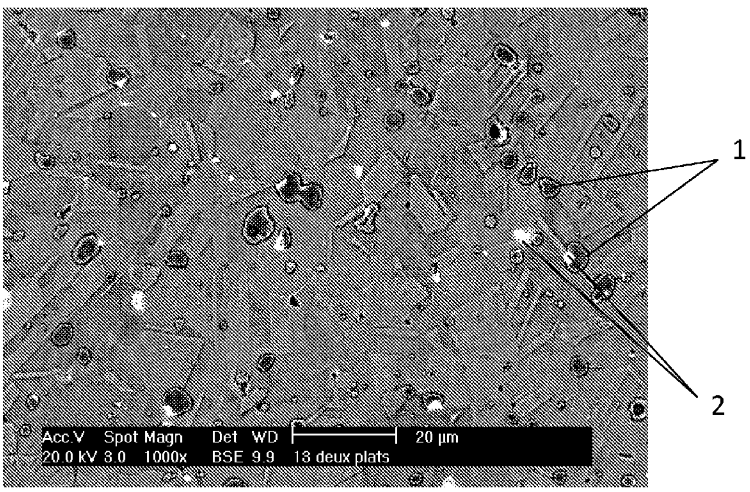

Fig. 1

(57) Abstract: Alloy containing between 1 % and 20% by weight of Ni, between 1 % and 20% by weight of Sn, between 0.5%, 3% by weight of Pb in Cu which represents at least 50% by weight of the alloy; characterized in that the alloy further contains between 0.01 % and 5% by weight of P or B alone or in combination. The invention also pertains to a metallic product having enhanced mechanical resistance at intermediate temperatures (300°C to 700°C) and excellent machinability. The metallic product of the invention can be advantageously used for the fabrication of connectors, electromechanical, or micromechanical pieces.

WO 2010/115462 A1

Machinable copper-based alloy and method for producing the same

Field of the invention

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.

Description of related 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 known heat-aging treatments 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. These alloys also offer good stress relaxation resistance, and high corrosion resistance in air.

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

These favorable properties, combined with good thermal and electrical 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 switches and electrical or electromechanical devices or as supports of electronic components or for making bearing friction surfaces subjected to high charges.

Good machinability in these alloys is usually obtained by adding lead, which is distributed as a fine dispersion of inclusions in the alloy matrix. Unfortunately such lead additions also increase markedly the alloy's warm shortness, which can lead to problems both in processing and in service.

The loss in ductility of Cu-based alloys at intermediate temperature (300°C-700°C) is a long-known problem and has been reviewed by R. V. Foulger and E. Nicholls, in "Metals Technology" 3, pages 366-369 (1976), and by V. Laporte and A. Mortensen, in "International Materials Reviews", in press (2009). The onset of grain boundary sliding in this temperature range results in the formation of voids and cavities at grain boundaries and changes the normally ductile fracture of copper and its alloys to intergranular brittle failure. This phenomenon was observed for pure copper but is much more pronounced when embrittling alloying or impurity elements are present in the alloy. At higher temperatures, exceeding this critical range, dynamic recrystallization can restore ductility.

The presence of molten Pb inclusions in such Cu-alloys can cause liquid metal embrittlement (LME), particularly at high strain rates. At the same time lead contents as low as 18 ppm were reported to embrittle grain boundaries of Cu-Ni alloys, and alloys that had been exposed to lead gas at 800°C have failed in a brittle manner, showing that lead can also cause solid-state grain boundary embrittlement; this is, contrary to LME, more severe at low strain rates. Other elements that are known to cause grain boundary embrittlement in Cu-alloys are sulfur and oxygen.

Brief summary of the invention

An object of the invention is therefore to propose a metallic product composed of a Cu-Ni-Sn-Pb-based alloy which overcomes at least some limitations of the prior art.

Another object of the invention is to provide a metallic product composed of a Cu-Ni-Sn-Pb-based alloy with enhanced tensile properties and having good machinability.

According to the invention, these objectives are achieved by means of a system and method comprising the features of the independent claims, preferred embodiments being indicated in the dependent claims and in the description.

These aims are also achieved by means of an alloy containing between 1% and 20% by weight of Ni, between 1% and 20% by weight of Sn, between 0.5% and 3% by weight of Pb in Cu which represents at least 50% by weight of the alloy; characterized in that the alloy further contains between 0.01% and 5% by weight P or B, alone or in combination.

In an embodiment of the invention, the alloy further contains between 0.01% and 0.5% by weight of P or B alone or in combination.

In a preferred embodiment of the invention, the alloy comprises 9% by weight of Ni, 6% by weight of Sn, 1% by weight of Pb.

The alloy of the invention is characterized by a yield strength $R_{p0.2}$ and a maximum stress R_m essentially above 180 MPa and 333 MPa, respectively, measured at 400°C after heat treatment at 800°C for about one hour, followed by a quench in water or in air. The alloy is also characterized by a Hv hardness essentially above 190, after a heat treatment at 800°C for about one hour and subsequent aging at 320°C for about twelve hours.

These aims are also achieved by a production method of a metallic product composed of the alloy of the invention and comprising the steps of: obtaining a first slug of said alloy having a homogeneous structure; annealing said alloy at a temperature comprised between 690°C and 880°C for homogenizing and improving the alloy cold forming properties; cooling at a cooling speed comprised between 50°C/min and

50000°C/min, depending on the transversal dimension of said product and composition of said alloy; and cold forming.

The present invention also encompasses a metallic product composed of the alloy of the invention and produced with the method of the invention, the product being characterized by mechanical resistance comprised between 700-1500 N/mm^2, a Hv hardness comprised between 250 and 400, and a machinability index greater than 70 %, in relation to standard ASTM C36000 brass.

The machinable metallic product can be fabricated without fissuring and has excellent mechanical and tensile properties at intermediate temperature (300°C-700°C).

In the present description of the invention, all % are expressed in % by weight even if not explicitly mentioned in the text.

Brief Description of the Drawings

The present invention will be better understood by reading the attached claims and the description given by way of example and illustrated by the attached figures, in which:

Fig. 1 represents a metallographic section of a B-containing Cu-Ni-Sn-Pb alloy according to the invention; and

Fig. 2 represents a metallographic section of a P-containing Cu-Ni-Sn-Pb alloy according to the invention.

Detailed Description of possible embodiments of the Invention

In an embodiment of the invention, Cu-based alloys comprise between 1% and 20% by weight of Ni, between 1% and 20% by weight of Sn, and Pb in a ratio that can vary between 0.1% and 4% by weight, the remainder being constituted essentially of Cu, with the unavoidable impurities being typically comprised in an amount of 500 ppm or less.

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 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. Consequently, in the alloy of the invention, lead content is preferably between 0.5% and 3% or 0.5% and 2% by weight, even more preferably between 0.5% and 1.5% by weight.

The alloy composition can optionally further comprise between 0.1% and 1% of an element such as Mn, introduced in the composition as deoxidizer. The Cu alloy can also comprise other elements, such as Al, Mg, Zr, Fe, or a combination of at least two of these elements, in place of Mn or in addition to Mn. The presence of these elements can also improve the spinodal hardening of the Cu alloy. Alternatively, devices preventing the Cu alloy from oxidizing can be used.

In another embodiment, part of the Cu content of the alloy of the present invention can be replaced by other elements, such as Fe or Zn, at a ratio for example up to 10%.

In yet another embodiment of the invention, the Cu-based alloy contains at least 0.01% by weight of an additional alloying element chosen among Al, Mn, Zr, P (phosphorus) or B (boron). Alternatively, the Cu-based alloy of the invention contains at least 0.01% by weight of a mixture of at least two additional elements chosen among Al, Mn, Zr, P or B.

In a preferred embodiment of the invention, the Cu-based alloy contains between 0.01% and 5% by weight of P or B.

In a more preferred embodiment of the invention, the Cu-based alloy contains 9% by weight of Ni, 6% by weight of Sn, 1% by weight of Pb, and between 0.02% and 0.5% of P or B.

The influence of addition of P and/or B on the mechanical properties at intermediate temperatures of Cu-Ni-Sn-Pb alloys was investigated. To this end, metallic products composed of a Cu-based alloy containing about: 9% by weight of Ni, 6% by weight of Sn, 1% by weight of Pb, and about between 0.02 and 0.5% of P or B, were prepared from pure constituents (pre-alloys Cu_3P and CuZr: 99.5% by weight, Al: 99.9% by weight, all others: 99.99% by weight) in a semi-continuous casting unit (capacity: 30kg) under a cover of argon.

The composition of the different alloys investigated, measured by inductively coupled plasma (ICP) analysis, is given in Table 1, where the compositions are reported in % by weight, and the balance is Cu. The value of Zr was not detectable with the ICP method.

		Ni	Sn	Pb	Al	Mn	Zr	B	P	Fe	Co
A1	CuNi9Sn6	8.907	6.230	1.025		0.002					0.004
A2	CuNi9Sn6Pb1	9.231	6.083			0.009					0.004
B1	CuNi9Sn6Pb1 + 0.5 Al	8.810	6.104	0.997	0.515	0.002					0.005
B2	CuNi9Sn6Pb1 + 0.5 Mn	8.960	5.979	0.968		0.474					0.005
B3	CuNi9Sn6Pb1 + 0.25 Zr	8.917	6.300	0.995		0.002	0.25			0.008	0.005
B4	CuNi9Sn6Pb1 + 0.3 B	8.950	6.096	0.963	0.020	0.002		0.325		0.016	0.18
B5	CuNi9Sn6Pb1 + 0.5 P	8.915	6.259	0.997		0.002			0.478		0.004
C1	CuNi9Sn6Pb1 + 0.03 B	9.480	6.250	0.890		0.003		0.02			
C2	CuNi9Sn6Pb1 + 0.1 P	9.170	6.300	0.920		0.027			0.075		

Table 1 – Composition of alloys

The metallic products were cast into cylindrical bars, 12 mm in diameter, and subsequently swaged in three steps down to a diameter of

7.5 mm. From these bars cylindrical tensile test samples having a gauge length of 30 mm and a diameter of 4 mm were machined. Samples were homogenized at 800°C for one hour in air and quenched in water.

Alloys C1 and C2 were added to this list in order to examine whether with a lower content of alloying additions the characteristics for machinability and high strength can be reached as well. In contrast to alloys denoted B, samples of alloys C1 and C2 were cooled in air after annealing at 800°C for 1 h.

Figs. 1 and 2 represent SEM micrographs of a metallographic section of the respectively B-containing (B4) and P-containing (B5) alloys, according to the invention. Both alloys B4 and B5 show hard second phase particles 1, rich in Ni, Sn, and either B or P respectively formed when B or P is added to the Cu-based alloy. Hard second phase particles 1 rich in Ni, Sn, and Zr are also formed (not shown) when Zr is added to the Cu-based alloy. The second phase 1 is harder than the rest of the Cu-based alloy matrix. Alloys B4 and B5 are also characterized by a grain size, here essentially 35 µm in average diameter, smaller by a factor near two than that in other alloys not containing B or P. The alloys C1 and C2 with the lower B or P content, respectively, also exhibit second phase particles 1 although in a decreased amount (micrograph not shown). The second phase particles 1 are distributed evenly in the microstructure and are few micrometres in size. Pb inclusions 2 appear in white in Figs. 1 and 2.

Table 2 reports Vickers hardness (HV10) test values measured for the alloys B1 to B5, after heat-treating at 800°C for about one hour and subsequent aging at 320°C for about 10 and for 12 h. The test values are compared with values obtained for the alloy A2. The highest increase in hardness was found for the alloys B4 and B5 according to the invention.

Time [h]	A2	B1	B2	B3	B4	B5
0	98	105	99	102	114	114
10	177	137	161	179	167	190
12	160	138	160	177	188	208

Table 2 - Vickers hardness (HV10) in Hv

In Table 3, yield strength ($R_{p\ 0.2}$) and maximum stress (R_m) values are reported for A1 to B5 alloy samples. The values were obtained by performing hot tensile tests after heat treatment at 800°C for about one hour, followed by a quench in water or in air. Tensile tests were conducted with a servo-hydraulic testing machine (MFL 100 kN) at 400°C at a strain rate of $10^{-2}\ s^{-1}$. The samples were heated rapidly using a lamp furnace (Research Inc., Model 4068-12-10), reaching the stabilised testing temperature within less than 2 min, so as to minimize the occurrence of phase transformations during the heat-up period. Due to both rapid heating and high strain rate, fracture of the samples was obtained after not more than three minutes' hold at 400°C.

	A1	A2	B1	B2	B3	B4	B5
$R_{p\ 0.2}$ [MPa]	229	161		-	166	184	190
R_m [MPa]	422	184	158	134	198	333	334

Table 3 - Yield strength ($R_{p\ 0.2}$) and maximum stress (R_m) in MPa

Lead added to CuNi9Sn6 alloy significantly embrittles the alloy. Improved yield strength ($R_{p\ 0.2}$) and maximum stress (R_m) values are obtained for alloys B4 and B5 of the invention compared to the values obtained for the other Pb-containing alloys A2 to B3 without P and/or B addition. Yield strength and maximum stress values obtained for alloys C1 and C2 with reduced amounts of B (0.03wt.%) and P (0.1wt.%), respectively 160 MPa and around 300 MPa at 400°C, were also improved compared to the values of alloys A2 to B3 at that temperature.

SEM investigations of longitudinal cuts of broken samples (not shown) of alloys C1 and C2, after fracture in the hot tensile tests above, showed that the second phase particles 1 are often situated adjacent to the Pb inclusions 2 (see Figs. 1 and 2) and that failure is intergranular, suggesting that fracture does not nucleate at the larger second phase particles 1.

Table 3 reports qualitatively the susceptibility to quench-crack formation of alloys A2 to B5. In Table 3, the sign "+" denotes the presence of cracks, with increasing number and depth going from "+" to "+++", while "0" stands for the absence of any cracks. Quenching experiments were performed on the as-cast alloy A2 to B5 samples by first heat treating the samples at 800°C for one hour and dropping the samples into a bath of water at room temperature, or of oil held at 80°C or alternatively at 180°C. Alloy sample surfaces were afterwards examined optically for cracks. Table 3 shows that the alloys B4 and B5 according to the invention are the least susceptible to quench-crack formation.

	water	oil 80°C	oil 180°C
A2	+++	++	+
B1	+++	+	+
B2	++	+	+
B3	+++	+	+
B4	+	0	0
B5	+	0	0

Table 3

The machinability characteristics of the alloys B4 to C2 according to the invention, tested by drilling, accounting for cutting speed, feed and chip length, were found to be similar to that of the other alloys not containing P or B. Alloy B5 was found to have best machinability characteristics compared to the other alloys of the group A1 to C2.

The above results suggest that the hard second phase particles 1 do not represent preferred nucleation sites for intergranular voiding in the alloy but rather impede grain boundary sliding, which is one of the principal reasons for intermediate temperature (300°C – 700°C) embrittlement in copper alloys, without nucleating voids. Moreover, in the Zr, B- and P-containing alloys (B3, B4, B5, C1, C2) of the invention, Pb inclusions 2 show a marked tendency to be situated adjacent to the solid B- or P-containing second phase precipitates 1, and have rather irregular, complex shapes. This can result in low energy interfaces between molten lead inclusions 2 and the hard second phase 1 at intermediate temperatures, such that Pb "wets" the second phase particles 1. This increases the applied stress necessary for the attainment of instability of molten Pb inclusions 3, delaying the fracture of the B- and P-containing alloy making it both stronger and more ductile, and possibly yielding improved tensile properties at intermediate temperatures. In other words, the added elements, such as P, B or Zr, in the Cu-based alloy cause the formation of the hard second phase 1 that presents, in contact with molten Pb, a low interfacial energy, such as to stabilize the particles against shape change under the application of stress. Higher tensile properties of B4 and B5 in comparison to A2 and the remaining B-series alloys (Table 2) can also be explained by the difference in grain size where both B and P acting as grain refiners, and load-bearing by the less ductile second phase 1.

Clearly, the alloys B4, B5, C1 and C2 of the invention solve, to a significant degree, the intermediate temperature embrittlement that is caused by the addition of lead to improve the machinability of the CuNi9Sn6 alloy. The leaded B3 to C2 alloys retain their attractive free-machining attributes.

In an embodiment of the invention, a machinable metallic product, composed of the Cu-based alloy of the invention, is obtained by a method comprising a continuous or semi-continuous casting process. In the method, a first slug is extruded, for example, to a diameter that can be comprised typically between 25 mm to 1 mm. The alloy is then cooled, for example, by a stream of compressed air or by water spray or any other suitable means able to reach a suitable cooling speed that is preferably sufficiently high to limit the formation of the fragilizing second phase and fast enough in order to prevent fissuring, as will be discussed below.

The material of the first slug then undergoes one or several cold forming operations, e.g. by rolling, wire-drawing, stretch-forming, hammering, or any other cold deformation process. After the cold forming step, a second slug is annealed, typically in a through-type furnace or removable cover furnace, at an annealing temperature that must lie within the range where the alloy is one-phased. In the case of the Cu alloy of the invention having one of the compositions described above, the annealing temperature is comprised between 690°C and 880°C. The annealing step, or heat homogenizing treatment step, is used, among other, to induce ductility, refine the structure by making it homogeneous, and improve cold forming properties of the alloy.

In a variant of the embodiment, the second slug can undergo an annealing or heat homogenizing treatment step prior to the cold forming process.

During the annealing step, at least partial recrystallization will occur with the second slug, where new strain-free grains nucleate and grow to replace those deformed by internal stresses. After the annealing step the second slug is cooled, again, at a cooling speed that is preferably sufficiently high to limit the formation of the fragilizing second phase and fast enough in order to prevent fissuring.

One or several successive steps of cold forming process can be performed, each cold forming step being followed by an annealing and cooling step, in order to obtain successive slugs having desired diameters and shapes.

After the successive cold forming, annealing and cooling steps, a final slug can be wire-drawn or stretch-formed to a final diameter and/or shape to obtain a machinable product. A spinodal decomposition heat treatment, or hardening, can then be finally performed on the machinable product or on the machined pieces in order to obtain optimal mechanical properties. The latter heat treatment can take place before or after the final machining.

The cooling step after the extrusion and/or annealing 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, but 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 slug, or 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. In the method of the present invention, cooling, after the extrusion and/or annealing steps, is performed at a cooling speed comprised between 50°C/min and 50000°C/min.

Copper-nickel-tin alloys have a long solidification interval leading to a considerable segregation during the casting operation. During the continuous or semi-continuous casting process, the molten alloy can be stirred in order to obtain a greater regularity for the cast metal, in respect to its surface state and its internal properties, such as segregation and shrinkage. Moreover, when the molten alloy is melted and cast, a dendrite structure is generated and a fine-grained alloy cannot be obtained.

The copper alloy can be stirred electromagnetically in order to agitate the melt. Such magnetic forces are able to produce sufficient stirring of the slug allowing for a reduction in the number of segregation centers and obtaining the Cu-based alloy having fine equiaxed crystals with average grain size being essentially below 5 mm.

Alternatively, the molten Cu alloy in the slug can be agitated mechanically using ultrasonic energy in order to produce cavitation and acoustic streaming within molten material. Other type of mechanical stirring can also be used such as forced gas mixing, and physical mixing such as oscillating or shaking the molten alloy, or mechanical devices such as a rotor, a propeller, or a stirring pulsing jet. Alternatively, the electromagnetic stirring can be used in combination with mechanical stirring or, the ultrasonic stirring can be used in combination with mechanical stirring.

In another embodiment of the invention, first slugs of the Cu-based alloy having a diameter up to 320 mm are produced using a sprayforming process, such as the process known as the "Osprey" method and described in patent EP0225732. Here, using atomized particle sizes in the size range of 1-500 microns, alloy with an average grain size below 200 microns could be obtained. The sprayforming method makes it possible to obtain an almost homogenous microstructure presenting a minimal degree of segregation. Other types of slugs, such as ingot, disc or bar having a rectangular section can also produced with the sprayforming process. The spraying of the molten metal or metal alloy particles is performed under a desired atmosphere, preferably under an inert atmosphere, such as Nitrogen or Argon.

Alternatively the metallic product can be obtained by a static billet casting method or any other suitable method.

The Cu-based alloy product is characterized by a tensile strength comprised between 700-1500 N/mm^2 (700-1500 MPa), measured at room temperature, after the annealing treatment and cooling steps; a Vickers hardness (HV10) comprised between 250 and 400, measured after the annealing treatment and cooling steps; and a machinability index greater than 70 %, in relation to standard ASTM C36000 brass. Moreover, the Cu-based alloy product can be machined easily due to the facilitated elimination of chips generated during turning and can be advantageously used for machining operations requiring, in particular, a turning step, or a free-cutting step, a stamping step, a bending step, a drilling step, etc.

The Cu-based alloy product of the invention can be advantageously used in order to obtain a product having the shape of rods, wires having circular or any other profile shape, strips, for example rolled strips, slabs, ingots, sheets, etc. The Cu-based alloy product can also be used advantageously for the fabrication of the whole or part of a machined piece, such as electrically conductive pieces having, for example, a high elastic limit above 700 N/mm^2, such as connectors, electromechanical pieces, parts in telephony, springs, etc., or micromechanical pieces in applications such as micromechanics, horology, tribology, aeronautic, etc., or any other pieces in diverse applications.

The method of the present invention makes it possible to produce a machinable Cu-Ni-Sn-based products containing up to several percent by weight of Pb and between 0.01% and 0.5% of P and/or B, without it fissuring during fabrication, and having excellent mechanical and tensile properties.

Reference Numbers and Symbols

1	second phase particle
2	Pb inclusions
$R_{p\ 0.2}$	yield strength
R_m	maximum stress

Claims

1. Alloy containing between 1% and 20% by weight of Ni, between 1% and 20% by weight of Sn, between 0.5%, 3% by weight of Pb in Cu which represents at least 50% by weight of the alloy; characterized in that the alloy further contains between 0.01% and 5% by weight of P or B, alone or in combination.

2. The alloy according to claim 1, wherein the alloy further contains between 0.01% and 0.5% by weight of P or B alone or in combination.

3. The alloy according to claims 1 or 2, wherein said alloy comprises 9% by weight of Ni, 6% by weight of Sn, 1% by weight of Pb.

4. The alloy according to claim 3, wherein said alloy has a yield strength $R_{p\ 0.2}$ essentially above 180 MPa, measured at 400°C after heat treatment at 800°C for about one hour, followed by a quench in water or in air.

5. The alloy according to claims 3 or 4, wherein said alloy has a maximum stress R_m essentially above 333 MPa, measured at 400°C after heat treatment at 800°C for about one hour, followed by a quench in water or in air.

6. The alloy according to any of the claims from 3 to 5, wherein said alloy has a Hv hardness essentially above 190, measured after a heat treatment at 800°C for about one hour and subsequent aging at 320°C for about twelve hours.

7. The alloy according to any of the claims from 1 to 6, wherein said alloy comprises a second phase (1) containing Ni, Sn, and either B or P

respectively, after a heat treatment at 800°C for about one hour, followed by a quench in water or in air.

8. Production method of a metallic product composed of the alloy characterized by any of the claims from 1 to 7, the method comprising the steps of:

a) obtaining a first slug of said alloy having a homogeneous structure;
b) annealing said alloy at a temperature comprised between 690°C and 880°C for homogenizing and improving the alloy cold forming properties;
c) cooling at a cooling speed comprised between 50°C/min and 50000°C/min, depending on the transversal dimension of said product and composition of said alloy; and
d) cold forming.

9. The method according to claim 8, wherein step a) of claim 8 is a continuous casting process for extruding a first slug of said alloy with a diameter comprised between 25 mm and 1 mm.

10. The method according to claims 8 or 9, wherein said alloy in first slug is stirred electromagnetically or mechanically in order to obtain said alloy with fine equiaxed crystals with average grain size being essentially below 5 mm.

11. The method according to claim 8, wherein step a) of claim 8 is a sprayforming process and wherein said first slug is formed with a diameter up to 320 mm and an average grain size below 200 microns.

12. The method according to any of the claims from 8 to 11, wherein said cold forming step comprises a rolling, wire-drawing, stretch-forming, hammering process.

13. Metallic product obtained from the method characterized by any of the claims from 8 to 12, wherein
said metallic product has a tensile strength comprised between 700-1500 MPa, measured at room temperature after the annealing and cooling steps b) and c) of claim 8.

14. The product according to claim 13, wherein
said product has a Hv hardness comprised between 250 and 400, after the annealing and cooling steps b) and c) of claim 8.

15. The product according to claims 13 or 14, wherein
said product has a machinability index greater than 70 %, in relation to standard ASTM C36000 brass.

16. The product according to any of the claims from 13 to 15, wherein
the product has the shape of a rod, wire, strips, slab, ingot, and sheet.

17. The product according to any of the claims from 13 to 16, wherein
the product is used for the fabrication of the whole or part of machined electrically conductive pieces or mechanical or micromechanical pieces.

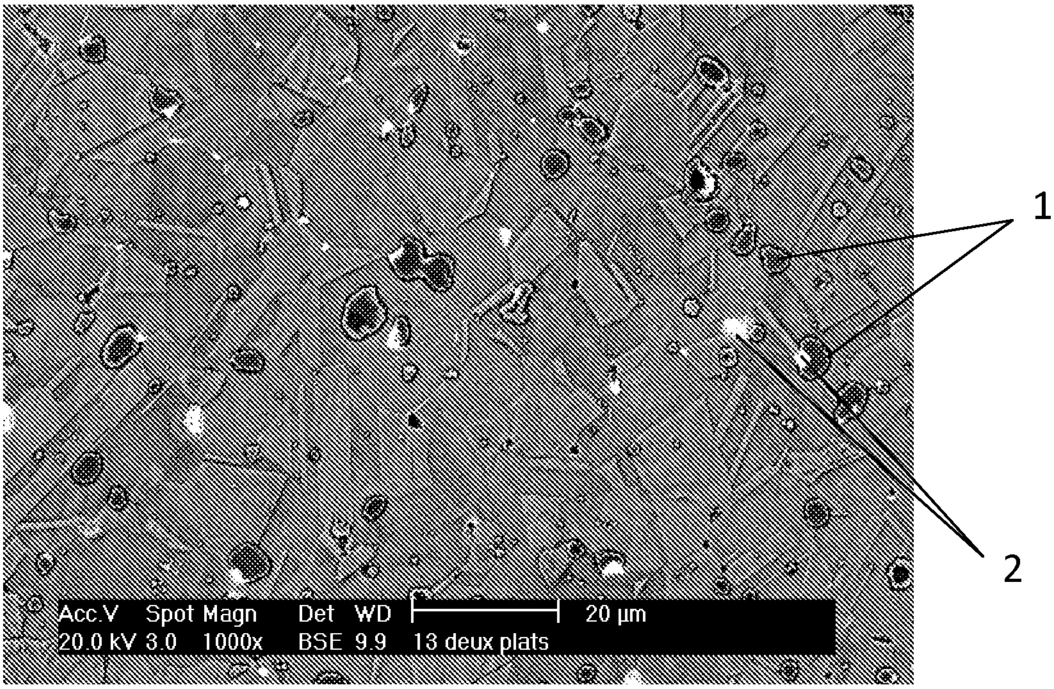
1
2
Acc.V Spot Magn Det WD 20 µm
20.0 kV 3.0 1000x BSE 9.9 13 deux plats

Fig. 1

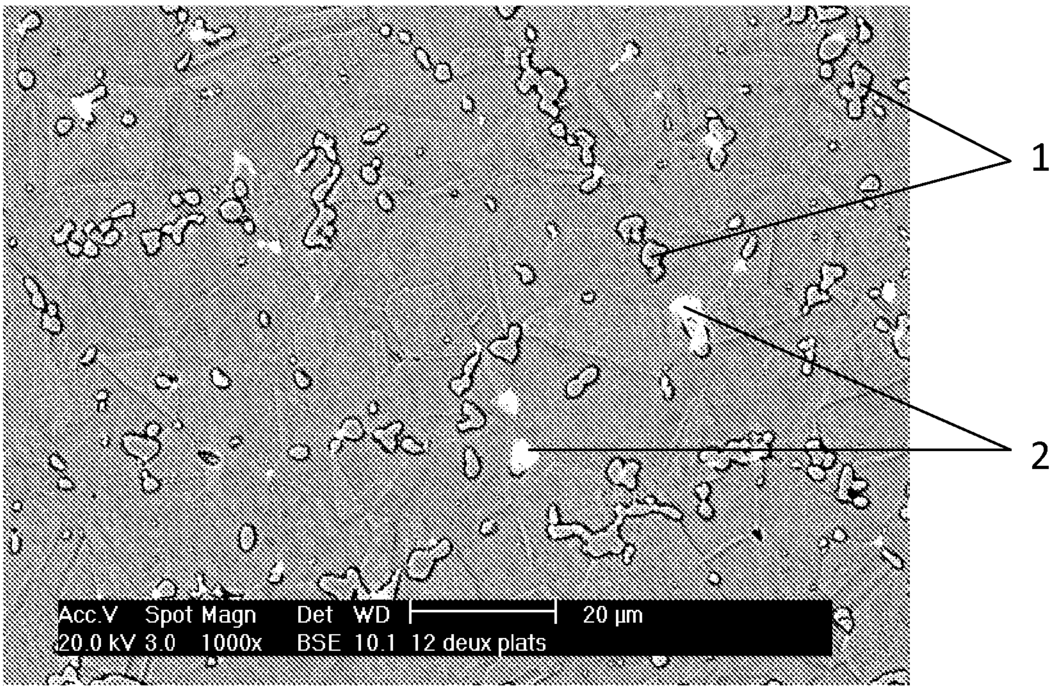
1
2
Acc.V Spot Magn Det WD 20 µm
20.0 kV 3.0 1000x BSE 10.1 12 deux plats

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/054250

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C9/02 C22C9/06 C22C1/02 C22F1/08
ADD.

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)
C22C C22F

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/089816 A1 (VINCENT EMMANUEL [CH]) 26 April 2007 (2007-04-26) paragraphs [0002], [0006], [0007], [0009], [0014], [0015], [0017], [0018], [0035], [0038] - [0049]; table 2	1-17
X	J.R. Davies (Editor): "ASM Speciality Handbook - Copper and Copper Alloys" 1 January 2001 (2001-01-01), ASM International , USA , XP002587020 ISBN: 0-87170-726-8 Pages 24, 181 and 182	1

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 June 2010	02/07/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Brown, Andrew

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/054250

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	V. LAPORTE AND A. MORTENSEN: "Intermediate Temperature Embrittlement of Copper Alloys" INTERNATIONAL METALS REVIEWS, vol. 54, 1 March 2009 (2009-03-01), pages 94-116, XP002587021 USA the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/054250

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		BR PI0418718 A	11-09-2007
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		CN 1961089 A	09-05-2007
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		WO 2005108631 A1	17-11-2005
		JP 2007531824 T	08-11-2007