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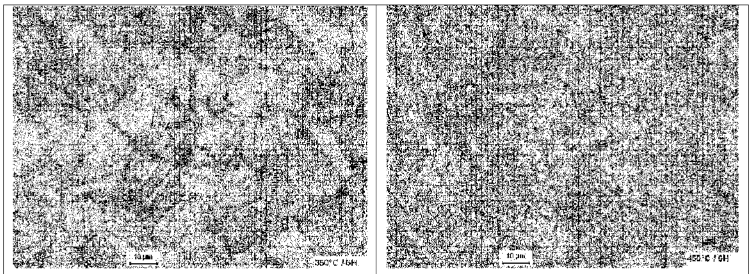

Fig. 1a  Fig. 1b

(57) Abstract: Precipitation hardened alloy on the basis of copper, zinc, nickel and manganese exhibiting a high strength and ductility with values similar to those of stainless steels in combination with excellent machinability. The inventive alloy family is characterized by fine fibre-like or globular precipitates that emerge during intermediate temperature annealing treatments, which in case of the unleaded variations significantly improves the machinability. The alloy of invention is particularly suited for free machining applications such as the production of pen tips and reservoirs for writing implements of reduced tip dimensions, where conventional Cu-Ni- Zn-Mn alloys fail due to lack of strength and where the corrosion resistance in gel-based inks is insufficient without restriction to other fields of application.

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# Cu-Ni-Zn-Mn alloy

## Field

**[0001]** The present invention generally relates to wrought Cu-Ni-Zn (nickelsilver) alloys, more particularly to Cu-Ni-Zn-Mn alloys mainly for the use in areas where machining operations are substantial.

## Description of related art

**[0002]** With regard to the current market situation the trend goes from ball point pens typically filled with oil-based inks of relatively high viscosity towards roller-ball pens with inks of lower viscosity. These new lower viscosity inks are mainly water-based gel-inks. Compared to oil-based inks, gel-inks have the advantage of allowing a greater variety of bright colors and can have glitter effects, as they usually contain pigments that sink into the paper. Driven by stylistic arguments and reducing the ink consumption the trend in writing instruments goes towards finer pens, which can be more easily be realized with low viscosity inks, in particular with roller-ball pens. Reducing pen tips to dimensions smaller than 1.6 mm diameters cause stringent consequences with respect to the strength of the tip material. In order that a tip can bear the same load with finer tip dimensions, higher strength values of the alloy must be assured. Therefore, so far only stainless steel have been used as tip material for the finest tips, while Cu-based alloys are regarded as not being suitable due to their inferior strength. Another common mistrust of Cu-Ni-Zn alloys compared to stainless steels is the resistance against corrosion in water-based gel inks. The invented alloys presented here aim to represent an alternative to stainless steel alloys used in pen tips, which show mechanical properties (strength and ductility) as good those of stainless steels and corrosion properties, which are suitable for pen tip applications, where gel-based inks are used.

**[0003]** Introduction

The alloy family Cu-Zn-Ni originally imported from China in 17$^{th}$ century has later in the 18$^{th}$ century been recognized almost parallel in France (1819), Germany (1823) and England (1832) as a copper-nickel-zinc alloy and given the names "Maillechort" – the later after their Lionese inventors Maille and Chorier, "Neusilber" and "Nickelsilver". In recent times nickelsilver is known for its good combination of properties and the silvery color has promoted the alloy to be successfully used in various applications. Today most commercially available Cu-Zn-Ni alloys contain between 10-25% Ni, which due to its complete solubility in Cu increases not only the strength of the alloy (by solid solution strengthening, see below) but also elastic modulus and the corrosion resistance. On the other hand, Cu-Ni-Zn alloys of grey color bear significant disadvantages, which are related to the effect of 'fire cracking' [H.W. Schläpfer, W. Form Metal Science 13 (1979); H.W. Schläpfer, W. Form Metall, 32, 135 (1978)] that is related to the high internal stresses in the pure mono-phased alpha alloys containing lead. The term fire cracking describes a kind of liquid metal embrittlement, which occurs in certain leaded alpha phase alloys, when cold deformed and annealed, whereby an explosive intergranular fracture occurs during or after the annealing process.

**[0004]** To circumvent this difficulty successive alloy development progress led to the partial replacement of Ni with Mn, which allowed to maintain the grey color, meanwhile changing the alloy from a pure alpha alloy to a duplex like alpha/beta structure, which is not prone to fire cracking as internal stresses are released at the phase boundaries. Mn has a more limited solubility in Cu than Ni, but can be alloyed up to approximately 15 wt.% in Cu-Zn alloys resulting similarly to Ni in a grey color appearance of the alloy (e.g. see US5997663).

**[0005]** Nowadays generations of Cu-Ni-Zn-Mn alloys often contain about 10-25 wt.% Ni, and 3-7 wt.% Mn. The field of applications ranges from writing instruments, to eye glass frames, keys, applications in watch industry, fittings, fine tooling applications and several other areas, where free-machining operations are frequent or inevitable resulting in large quantities of waste material in form of chips (up to 50 %). Commonly lead in quantities of 1.0 to 3.0 wt.% are alloyed to alloys, where free-machining operations are required, which significantly improving their machinability.

**[0006]** Lead-free alloys

Pressured by new legislations demanding for environmentally friendly and nontoxic element additions the demand for lead-free products in particular in applications of free-machining is constantly increasing. As a consequence new solutions have to be found in order to secure the recycling path of Cu-based alloys containing lead substituting elements

**[0007]** The most prominent current alternatives to Pb as a chip breaker in free-machining Cu-alloys are: Bismuth, Silicon and Tellurium. Bismuth has similar properties and behaviour with Cu-alloys as lead, i.e. low melting point (Pb: 327°C, Bi: 271°C), miscible in the liquid and immiscible in the solid, high density (Pb: 11.3 g/cm$^3$, Bi: 9.78 g/cm$^3$), a lubrication effect during machining and so represents an excellent chip breaker as is Pb. However, due to the incompatibility of Bismuth with certain Cu-based alloys (high internal stress causing stress corrosion cracking) a replacement of Pb with Bi in die-castings and wrought products is not recommended. Alloys containing bismuth are also more difficult to recycle, because recycling is done unmixed and so far fully developed recycling does only exist for lead containing copper alloys [Adaptation to Scientific and Technical Progress of Annex II Directive 2000/53/EC; J. Lohse, S. Zangl, R. Groß, C.O. Gensch, O. Deubzer. Öko-Institut e.V. (2008)]. Bismuth is industrially rated as less toxic than lead and other neighboring heavy metals, however injection of large doses can cause kidney damage. Furthermore, it is considered that its environmental impact is small, due in part to the low solubility of its compounds [http://en.wikipedia.org/wiki/Bismuth; Fowler, B.A.. "Bismuth" in Friberg, L.. *Handbook on the Toxicology of Metals* (2nd ed.). Elsevier Science Publishers. (1986),117]. Nonetheless bismuth has found its way into brass products as chip breaker mainly in Asia. Several patents describe the effect of Bi as a chip breaker in free-machining wrought copper alloys [US5167726; EP1790742].

**[0008]** Alternatively, silicon has been suggested, as an element addition to favor chip breaking in brasses, but is due to the less-favorable chip form, the absence of a self-lubricating effect causing higher wear damage on tools and the associated difficulty to recycle such chips neither an easy choice for a free-machining Cu-based alloy. Furthermore the risk of Fe-Si precipitates during casting of brasses containing low Fe concentrations further reduces the machinability. Silicon containing free-machining brasses, which show high strength levels than Si-free leaded versions of free-machining brasses are nowadays available and are covered in large parts by the patent family [EP1038981; EP1452613]. Apart from its effect on machinability Silicon has the strongest influence in the Cu-Zn diagram to shift the phase boundary between alpha and alpa+beta towards the beta rich side (Guillet Zn equivalent of 10; see: [L. Guillet and A. Portevin, Revue de Metallurgie Memoirs XVII, Paris, (1920), 561]) and has a positive influence on the strength, wear resistance and corrosion resistance.

**[0009]** Other known alternative Pb replacements in copper alloys are based on additions of Tellurium, Calcium and Graphite acting in form of intermetallics or particles as chip breakers [WO2008/093974; WO9113183]. Copper Tellurium alloys (C14500) contain 0.4-0.7 wt.% Te with minor additions of P and Ag and the rest being Cu. They form CuTe-intermetallics with a satisfactory chip breaking effect. Unfortunately, the alloy is not an easy to manufacture alloy due to the high sensitivity of forming oxides causing embrittlement. In addition, in brasses, Te forms brittle ZnTe intermetallics as well results in unfavorable properties. Graphite containing Cu-alloys are expensive due to high production cost via spray casting technology. Little or no information is available on Ca-containing Cu-alloys [WO2008/093974], in particular with respect to Cu-Ni-Zn or Cu-Ni-Zn-Mn alloys.

## Summary

**[0010]** It is part of the aim of this invention to introduce new microstructural design solutions for the alloy, which allows having, even in the absence of lead as a chip breaker, good machinability performances in free-machining operations. This can be solved on the one hand by adjusting the microstructure related to its partitioning of the alpha/beta phases and/or by additions of minor alloying elements forming precipitates with one of the major alloying elements. The minor alloying elements foreseen for this task are Fe, Al, Ca, Sn, P, and Si. Although it is known, that duplex structures, or precipitates favor chip breaking compared to a monophase structure, our multi-path approach is new with regard to the field of application as well as the alloy family of Cu-Ni-Zn-Mn alloys. First mentioned approach in the invention relating to the fine needle like precipitates of beta or beta′ phase in alpha mother grains is conceptually new and can be applied not only to this alloy family, but basically all Cu-Zn alloys, where part of the microstructure is in a metastable condition with respect to the phase transformation. The second approach of using precipitation of supersaturated solutions is a well-known process to increase the strength, but here it fulfills for this specific family of alloys and specific application two tasks: hardening and chip breaking and thus can be considered as novel. Lastly adding Ca as chip breaker has so far not found notation in combination with the fields of applications and the alloy family considered mentioned here.

**[0011]** Conventionally, there are four different hardening mechanisms known in single phased metals: Precipitation hardening, cold deformation hardening, solid solution strengthening, and grain size strengthening (Hall-Petch strengthing). Industrially mainly the first two mechanisms are of importance. Precipitation hardening is typically used in low-alloyed Cu-alloys where high electrical conductivity paired with moderate strength is requested. Spinoidal decomposition can be regarded as a special variation of precipitation hardening out of a supersaturated solid solution and finds application in Cu-alloys mainly in alloys containing substantial amounts of Sn or Ti. Cold deformation hardening is typically used for increasing the strength in rods, profile and wire products independent of the type of alloys. Solution hardening can be regarded as a side-effect when adding additional elements for improving different properties of the alloys, but is as such not of great relevance. Finally grain size hardening is industrially and technically difficult to control and its hardening contribution becomes evident only at grain sizes smaller than about 10 micrometers, sizes difficult to achieve in industrial production.

[0012] Similar to duplex steels, brasses or nickel-silver alloys having a certain range of Zn content exhibit a duplex alpha (face-centered cubic, fcc) and beta (body-centered-cubic, bcc) structure, which apart from representing a fifth mode of increasing strength, is also beneficially influencing the machinability, grain size stability and hot workability. Current commercially available leaded Cu-Ni-Zn-Mn alloys range in the Ni content from 5 to 25 wt.%, a Mn 0-7 wt.%, Zn 25- 40 wt.% and rest Cu and impurities typically < 1 wt.%. According to Guillet's rule [L. Guillet and A. Portevin, Revue de Metallurgie Memoirs XVII, Paris, (1920), 561] Mn shows with a factor of 0.5 only a slight influence towards the beta rich side in the phase diagram, while Ni exhibits a factor of -1.2 keeping the phase diagram on the alpha-rich side, and thus almost in balance for a Mn content of 6 wt.% and Ni content of 12 wt.%. Thus, as a first approximation the complicated 4 component system Cu-Zn-Ni-Mn can in this case be treated as the Cu-Zn binary phase diagram. However, as shown below for more precise estimates on a multicomponent phase diagram, more advanced thermodynamic software tools are required. With increasing Ni and Mn content the strength increases. Typical tensile strength values for cold drawn materials are 700 - 800 MPa, while in fewer cases values up to 900 MPa can be found for strongly cold drawn wires, however that typically goes at the expense of ductility, so that tensile elongations are limited to ~1%.

[0013] In this application we aim to combine these mechanisms in a novel family of Cu-Ni-Zn-Mn alloys in such a way, that high strength and sufficient ductility can be achieved. Hereto the Zn, Al, Ca, Mn, Si, Ni, Sn, Fe content is adjusted to have a sufficiently high beta content at elevated temperatures, which can be later reduced by thermo-mechanical heat treatments for increasing the cold deformability, followed by a precipitation hardening process, where on the one hand fine precipitates of beta or beta´ (tetragonal distorted bcc structure) are nucleating in alpha-mother grains, while on the other hand intermetallic precipitates are forming. This yields a strong increase in tensile strength higher than usually reached in Cu-Ni-Zn-Mn alloys. In these classical compositions a trade of is required between cold deformability, which increases the strength and the ductility which remains. Here however, the strengthing is only in part resulting from cold deformation (increase in dislocation density and point defects), but from the precipitation strengthening. Thus in final processing steps only moderate deformation has to be applied, reaching much higher strength values with still good plasticity. The following detailed description of the invention addresses the above mentioned points in more detail.

**[0014]** Corrosion properties

Dezincification is understood as the dissolution of Zn in Cu-Zn alloys and can be regarded as the most severe corrosion effect in Cu-alloys. More precisely Zn dissolves by a di-vacancy diffusion process leaving a "hole" in the crystal lattice of the surface layers [J.Y. Zou, D.H. Wang, W.C. Qiu, Electrochmica Acta, 43, (1997), 1733-1737]. Thus, Cu-alloys free of Zn show superior corrosion resistance than brasses. In analogy, alpha brasses are more corrosion and dezincification resistant than the Zn-rich beta-brasses. Cu-Ni-Zn alloys show in comparison to brasses similar corrosion resistance as alpha brasses, but have due to the higher nickel content a better tarnish resistance and resistance to stress corrosion cracking. Little information is available on the corrosion properties and the influence of minor alloying elements in Cu-Ni-Zn alloys, but can be extrapolated from the effects known to brasses. There different alloying elements have been reported to improve corrosion resistance and retard dezincification in brasses as summarized in Ref. [D.D. Davies, "A note on the dezincification of brass and the inhibiting effect of elemental additions", Copper Development Association Inc., 260 Madison Avenue, New York, NY 10016, (1993), 7013-0009]. Minor additions of arsenic, phosphorous or antimony are known to show improved corrosion resistance in all-alpha brasses. Duplex brasses where the beta phases are completely enclosed by alpha grains do exhibit also a beneficial effect on the resistance to dezincification. Al-containing alpha brasses are well known to show improved corrosion resistance (Admiralty or Naval brasses) and even dezincification in duplex brasses was reported to be retarded when adding up to 2 wt.% Al. The influence of tin on the dezincification and corrosion of brasses is more ambiguous as it has a positive effect in beta but a negative effect in alpha grains. However in combination with Al additions an amount of up to 1 wt.% Sn has been reported to improve corrosion and dezincification resistance. Silicon exhibits a positive effect when added below the level of precipitation of Si-rich precipitates in alpha grains of brasses, which lies at around 0.5 wt.%. Above this level of Silicon corrosion and dezincification increases as it does for iron additions. Finally the influence of lead shows positive effects in alpha brasses, but only if Pb-compounds are forming a passivation layer [S. Kumar, T.S.N. Sankara Narayanan, A. Manimaran, M. Suresh Kumar, Mater. Chem. & Phys.106, (2007), 134–141], while it shows reducing performance in duplex brasses.

**[0015]** The present invention aims also for applications where corrosion properties can be of crucial importance, in particular in solutions where crevice conditions are present. This is for instance the case in ball pen tips where the gap between the ball and the surrounding pen socket is of the order of few micrometers distance and the ink is not constantly stirred (during storage of the pen tip). In water-based gel-inks this may locally lower the pH of the ink and cause local corrosion attack. The right choice of elements and the appropriate microstructure to reduce corrosion is thus detrimental to the lifetime of a pen tip.

**[0016]** More generally the invention also aims to increase the dezincification and the corrosion resistance in mild and medium active solutions to levels which are common to stainless steels, with the goal to replace them in applications, where a combination of high strength, good corrosion resistance and improved machinability are the main parameters for the materials choice.

**[0017]** The invention relates to age hardenable high-strength Cu-Zn-Ni-Mn-based alloys with superior mechanical properties and excellent machinability suitable for applications, where intensive free-machining operations are required as for example for the production of pen tips and reservoirs for writing implants of reduced tip dimensions. However, the range application goes beyond the production of writing instruments and does in general extent to all applications where heavy free machining operations are required. The composition of the invented alloy is given as follows:

Cu: 42 – 48 wt.%
Zn: 34 – 40 wt.%
Ni: 9 – 14 wt.%
Mn: 4 – 7 wt.%
Pb: 0 – 2.0 wt.%
Al: 0 – 1 wt.%
Sn: 0 – 2 wt.%
Fe: 0 – 0.5 wt.%
Si: 0 – 1.0 wt.%
Ca: 0 – 1.5 wt.%
As: 0 – 0.15 wt.%
P: 0 – 0.3 wt.%

**[0018]** The invention of the alloy aims to satisfy the current needs for lead-free machinable Cu-Ni-Zn-Mn alloys suitable free-machining operations as required for example in writing applications. In addition, the invented alloys exhibit an attractive combination of high strength with sufficient ductility required for subsequent operations or safety margins. While the flow stress reaches values comparable to those of typical stainless steels used for pen tip and other free-machining applications, sufficient cold-formability is often still required in order to perform further bending operations or other cold-deformation steps, such as the insertion of the pen ball onto the tip socket. However, in contrary to stainless steels the machinability of this alloy family is superior due to the precipitation hardened phases. Additions of arsenic as well as minor additions of P, Si, Al and Sn demonstrate beneficial effects on the corrosion resistance.

**[0019]** The copper alloy disclosed herein exhibits machinability performance (easier chip handling, less tool consumption) superior to that of stainless steel used in pen tip and also other applications allowing for a higher production rate of parts per hour. When subjected to a special low-temperature heat treatment, the alloy has a unique microstructure, which even in absence of lead, is leading to a good machinability performance superior to that of typical stainless steels used in pen tips. The alloy that is an ecologically friendly, lead-free free-machining Cu-Ni-Zn-Mn alloy free of harmful elements.

Brief Description of the Drawings

**[0020]** The invention will be better understood with the aid of the description of an embodiment given by way of example and illustrated by the figures, in which:

Fig1 shows an optical microscopy images of samples heat treated at 350°C (Fig. 1a) and 450°C (Fig. 1b) of alloy N° 1;

Fig. 2 shows an optical image of the longer screw-like chips of alloy N° 1 produced with the Citizen long turning machine;

Fig. 3 shows an optical microscopy images of the as-cast structure (Fig. 3a) and the cold deformed annealed (450°C) (Fig. 3b) of alloy N° 3;

Fig. 4 shows pseudo-binary phase diagram (Fig. 4a) and phase fraction diagram for a specific composition (Fig. 4b) of alloy N° 3.

Fig. 5 represents a screw-type and curly type chips shown for two types of alloys of the alloy N° 3;

Fig. 6 shows machining tests with Mikron Multistar made at 100 Hz on alloy N°3 with composition A annealed at 450°C (Fig. 6a and 6b); and alloy N°:1 (Fig. 6c and 6d), chip length of the leaded alloy N°:1 being smaller than that in alloy N°3;

Fig. 7 shows as-extruded microstructure (Fig. 7a) and after 2 cycles of cold deformation and annealing at 650°C) (Fig. 7b) of alloy N° 5; heat treated alloy at 540°C followed by 350°C (Fig. 7c) and 400°C (Fig. 7d) low temperature heat treatment of alloy N° 5; and

Fig. 8 shows optical microscopy image of a sample annealed at 540°C followed by a second annealing process at 400°C (Fig. 8a); secondary electron microscopy image of alloy with NiSn preciptates in beta phase matrix and at boundary to alpha grains (Fig. 8b) both of alloy N$^{o}$: 6.

Detailed Description of possible embodiments of the Invention

**[0021]** The present invention generally relates to wrought Cu-Ni-Zn (nickel-silver) alloys, more particularly to Cu-Ni-Zn-Mn alloys mainly for the use in areas where machining operations are substantial. The present invention relates also to leaded, leadless or lead-free free-machining Cu-Ni-Zn-Mn alloys particularly suited for applications in areas where free machining operations are heavily involved, such as writing instruments, eye glass frames, medical tools, electrical connectors, locking systems, fine tooling, fasteners and bearing for automotive industry, without restriction to other fields of application. In addition, the present invention aims to replace wrought steel products in various applications where high strength and sufficient ductility combined with excellent free-machinability are required with or without the presence of lead.

**[0022]** The present invention has among the above mentioned various fields of applications particular focus on writing instruments, where the tip material is in direct contact with the ink and the ball material. Nowadays a number of ball materials, such as various types of tungsten carbide hard-metal balls with different binders (Co, Co+Ni+Cr), different types of steels and different types of ceramic balls are on the market, while the type of inks can be separated into mainly gel-based and oil-based inks and to a lesser extent inks based on other liquids. The Cu-Ni-Zn-Mn alloy family presented here can be combined with all possible combinations of ball or ink materials.

**[0023]** The objective of the present invention is to provide a new high-strength Cu-Ni-Zn-Mn alloy family that thanks to a special thermo-mechanical treatment and an optimized alloy composition reaches mechanical properties comparable with those of wrought stainless steel alloys. The leaded variations exhibit excellent machinability and are thus promising candidates for all applications, where high strength, good ductility and excellent machinability are of utmost importance, i.e. writing instruments, eye glass frames, keys, applications in watch industry, fittings and other fine tooling and free-machining applications, without restricting other fields of application. The lead-free variations persuade on the one hand by their duplex alpha beta structure, and on the other hand by the precipitates both result in a significant improvement of the machinability with respect to untreated Pb-free Cu-Ni-Zn-Mn alloys. In addition, the lead-free variations do not contain any user unfriendly amounts of elements, which either may be harmful for human and/or environment.

**[0024]** The present invention is realized by providing seven different Cu-Ni-Zn-Mn alloys on a basis of copper, zinc, nickel, manganese and other elements. The compositions of the alloys presented here and in the granted patent family EP1608789B1 are optimized for special applications, where apart from production costs the appearance of the alloy is as important as the mechanical properties, machinability and corrosion properties. Different dimensions and geometrical forms can be produced from these alloys, such as wires, strips, rods, tubes and various profiles and square shapes. In particular wire drawn products such as pen tips for writing instruments are addressed, which after a hot deformation process are typically drawn down to the final diameter in successive cold drawing and heat treatment steps. In this respect the Mn content of the alloy is limited to the range of 4 – 7 wt.%. Higher levels of Mn show a negative effect during cold-forming, while a lower Mn content increases the risk of fire cracking and too low beta content during warm extrusion processes. Apart from the high cost of Ni, a higher Ni content (>14 wt.%) is pushing the phase diagram towards a purely mono-phase alloy even at elevated temperatures. A lower Ni content (< 9.0 wt.%) bears the risk that the silvery color turns gradually into a yellowish one and has to be increased in Cu content in order to maintain the balance between alpha and beta phases. In cases where steels are aimed to be substituted a silvery appearance of the Cu-Ni-Zn-Mn alloys is of great importance. The Zn content is chosen in a range that allows to vary the microstructure (fraction of beta content) from 0% to approximately 50% ± 10%. Zn content > 40 wt.% show a to high amount of beta suitable for cold drawing, while a lower content than 34 wt.% makes hot extrusion processing difficult. The content of Pb is kept at a minimum level to assure good to excellent machinability. The copper alloy is of grey or silver color / appearance typical for Cu-Ni-Zn-Mn alloys sometimes having a nuance of a pale yellowish tone.

**[0025]** For the alloys presented in this invention a thermodynamic model approach has been applied in order to have a better estimate on the phase fields and the influence of alloying elements on the phase fields than it is possible with the Guillet role of thumb used in brasses [J. Ågren, F. H. Hayes, L. Höglund, U.R. Kattner, B. Legendre, R. Schmid-Fetzer: Applications of Computational Thermodynamics. *Z.Metallkunde* 93, (2002), 128-142]. This is clearly a more refined approach than common alloy design approaches and has demonstrated to be a fine tool to evaluate the stability of each phase as a function of temperature.

**[0026]** The machinability of most of the alloys described below has been measured on a Citizen long turning lathe and a Mikron Multistar turning machine. The following machine parameters have been used: (see Table 1).

**[0027]** <u>First alloy:</u>
The first alloy is based on the granted patent EP1608789 applications and consists of 42 – 48 wt.% Cu, 34 – 40 wt.% Zn, 9 – 14 wt.% Ni, 4 – 7 wt.% Mn, ≤0.5 wt.% Fe, ≤0.03 wt.% P and ≤2.0 wt.% Pb.

**[0028]** Said granted patents mentioned above are based on the idea that thanks to a special thermal heat treatment an alloy with an alpha-beta structure stable at elevated temperature and thus suitable for hot deformation processes can be modified into a pure alpha alloy when annealed at temperatures between 630-720°C resulting in improved cold formability and better corrosion resistance due to the mono-phased structure. The associated chemical variations of the major elements are balanced out in order to guarantee the said microstructural transformation from a duplex to a mono-phase alpha alloy. According to Guillet's rule of thumb for the Zn equivalent in brasses, Mn is almost insensitive to the variation, while Ni is showing an alpha stabilizing effect. Our thermodynamic calculations in the multi-component system shows that for minor elements such as Fe a content of 0.5 wt. % increases the beta phase fraction of the alloy by about ~5-10%, without changing the slope of the curves, while at intermediate temperatures of about 400°C Fe provokes a co-existence of the gamma phase (< 5 % volume fraction) in an alpha/beta matrix. Phosphorous is added in order to increase the corrosion resistance.

| Citizen | | | | | | |
|---|---|---|---|---|---|---|
| Parameter | I | | II | | III | |
| Turning speed [1/min] | ~4'000 | | ~8'000 | | ~10'000 | |
| Lengthwise depth [mm] | 0.01 | | 0.02 | | 0.02 | |
| Facing depth [mm] | 0.01 | | 0.01 | | 0.01 | |
| Interpolation [mm] | 0.001 | | 0.001 | | 0.001 | |
| Cutting speed [m/min] | 25 | | 40 | | 50 | |
| | | | | | | |
| Mikron Multistar | | | | | | |
| Frequency [Hz] | 85 | | 95 | | 100 | |
| Turning speed [1/min] | ~16'000 | | ~18'000 | | ~19'000 | |
| Parts per minute | 120 | 140 | 120 | 140 | 120 | 140 |
| Feed | moderate | high | Low-moderate | moderate | Low-moderate | low |

**Table 1:** Machining test parameters used for the alloys included in the present invention.

**[0029]** The first invention presented here builds-up on the processing parameters used for the above mentioned granted patents, i.e. EP1608789, which allow the formation of a mono-phase alpha Cu-Ni-Zn-Mn alloy. Its primary aim was to develop an alloy suitable for pen tip applications, where the corrosion resistance is superior with respect to duplex phased Cu-Ni-Zn-Mn alloys. This can only be guaranteed in purely mono-phase state not allowing for microstructural conditions allowing galvanic corrosion leading to localized microstructural determined crevice conditions.

**[0030]** Compared to aforementioned alloys developed in the patent family EP1608789, the alloy presented here is in addition subjected to heat treatments at lower temperatures of 300-450°C (also called "low temperature heat treatment" below) allowing for a fine precipitation of beta and/or beta´ precipitates. This precipitates are showing a needle like morphology and are oriented along the primary crystallographic axis of the fcc mother grains. Figs. 1a and 1b shows micrographs with the low temperature heat treated alloys having fine precipitates of beta´ and beta, respectively. Note that the phase boundary between beta and beta´ (its tetragonal distorted variation) lies between 400 and 450°C. More particularly, Figs. 1a and 1b shows samples heat treated at 350°C (a) and 450°C (b) of alloy Nº 1.

**[0031]** It must be mentioned that the concept of low temperature heat treatments is commonly applied to Cu-alloys that are age hardenable, i.e. where a supersaturated solid solution is present with minor additions of elements. Here on the other hand not a chemical driving force for precipitation is used, but the energy difference between the beta and beta´ phase. This is often applied to steels, where a martensitic transformation causes an increase in the strength of the alloy. In this invention, this concept has been adopted, whereby the transformation cannot be induced by plastic deformation.

**[0032]** In order to determine the precise temperature range of heat treatments a special thermodynamic software tool has been applied, which allows calculating the phase stability fields in a multi-component system as a function of temperature and chemical composition [J. Ågren, F. H. Hayes, L. Höglund, U.R. Kattner, B. Legendre, R. Schmid-Fetzer: Applications of Computational Thermodynamics. *Z.Metallkunde* 93, (2002), 128-142].

**[0033]** Said alloy results in improved hardness and tensile strength of 850 – 950 MPa with remaining elongation levels of 2-10 % compared to the same alloy not subjected to the low temperature heat treatment (see Table 2). Even higher strength and ductility might be reachable by further optimization of thermo-mechanical treatment as it was done for unleaded alloys (see further down).

**[0034]** The machinability of said alloy exhibits thanks to the higher strength, the uniform partition of lead particles and the fine beta precipitates an excellent machinability (> ~90% with respect to CuZn39Pb3 = 100%), which makes it an interesting candidate for replacing stainless steels in pen tip applications. Most often chips were very short (< 1mm length) in particular when machining with the Mikron Multistar (at all conditions set in Table 1). But also favorable screw-shape chips.

**[0035]** Fig. 2 shows an optical image of the longer screw-like chips of alloy N° 1 produced with the Citizen long turning machine.

**[0036]** Second alloy

The second alloy of the present invention has a very similar chemical composition as the first mentioned alloy, however including arsenic, i.e. of 42 – 48 wt.% Cu, 34 – 40 wt.% Zn, 9 – 14 wt.% Ni, 4 – 7 wt.% Mn, ≤0.5 wt.% Fe, ≤0.03 wt.% P, ≤2.0 wt.% Pb and 0.01 – 0.15 wt.% As.

**[0037]** The second invention presented here builds-up on the processing parameters used for the above mentioned granted patents, i.e. EP1608789, which allow the formation of a mono-phase alpha Cu-Ni-Zn-Mn alloy.

**[0038]** Apart from Arsenic, the same influences on the variations of chemistry are present in this invented alloy as in the first alloy presented above.

**[0039]** As mentioned in the background to the invention, As is used in brasses as a corrosion inhibitor, which due its fast diffusion in alpha brasses migrates to the di-vacancies and inhibits further corrosion of the surface layer [J.Y. Zou, D.H. Wang, W.C. Qiu, Electrochmica Acta, 43, (1997), 1733-1737]. In the Cu-Ni-Zn-Mn alloy presented here, the presence of As also improves the corrosion resistance, which shows in aqueous solutions with < 1 wt. % NaCl and in water-based inks an increased corrosion potential and a lower corrosion rate as compared to the alloy without the addition of As. This in turn has also a positive effect on the ink, as fewer ions are taken up by the ink, which might lower their performance.

| Annealing temperature [°C] | **Vickers hardness [Hv5]** | | | | |
|---|---|---|---|---|---|
| | 6h | 1h | 5h | 10h | 24h |
| **Initial (650)** | 240 | | | | |
| | 239 | | | | |
| **350** | | 249 | 265 | 272 | 265 |
| **350** | | 253 | 260 | 268 | 265 |
| **400** | | 244 | 253 | 239 | 232 |
| **400** | | 241 | 254 | 239 | 234 |
| | | | | | |
| | Tensile tests | | | | |
| | Yield strength | Ultimate tensile strength | Total elongation | | |
| | [MPa] | | [%] | | |
| **650°C, 2h ; Ø 2.3 mm** | 177 | 453 | 47 | | |
| **450°C, 6h ; Ø 2.3 mm** | 537 | 730 | 14 | | |
| **350°C, 6h ; Ø 2.3 mm** | 738 | 815 | 7.3 | | |
| **450°C, 6h ; Ø 1.6 mm** | 663-681 | 858-877 | 7-9 | | |
| **450°C, 6h + 350°C, 6h ; Ø 1.6 mm** | 734 | 941 | 4 | | |

**Table 2:** Vickers hardness tests on samples annealed at 350 and 400°C for 1, 5, 10 and 24 hours compared to normal annealing temperatures for recrystallisation.

**[0040]** The low level As additions does not exhibit any difference in the microstructural appearance of the alloy and it exhibits the same mechanical properties and machinability performance as the version without As (First alloy).

**[0041]** Third alloy

The third alloy of the present invention is unleaded and contains the following chemical composition: 45 – 48 wt.% Cu, 37 – 40 wt.% Zn, 9 – 14 wt.% Ni, 4 – 7 wt.% Mn, ≤0.5 wt.% Fe, ≤0.03 wt.% P, ≤0.15 wt.% As and ≤0.1 wt.% Pb.

**[0042]** One aim of the present alloy invention was to increase the beta content of the microstructure to a level, which shows good machinability suitable for turning operations. This is realized by an increased Zn content as compared to the alloy composition of the first and second alloy of the present invention. Fig. 3a shows the as-extruded microstructure of the duplex phased alloy.

**[0043]** A second goal of the invention of this alloy was to increase the mechanical properties of the alloy by low temperature heat treatment steps during wire cold deformation. Fig. 3b shows the microstructure of such a cold deformed and annealed microstructure, where a heat treatment of 450°C has been applied.

**[0044]** Zn content below 37.5 % reduces the amount of beta during hot extrusion (~800°C) to a volume fraction close to zero percent, while with a content of Zn > 39% the beta phase fraction reaches about 30% at this temperature. However at lower temperature annealing its content increases to almost 50% and thus reduces the ability to strongly cold deform the material. Increasing the Mn content and reducing the Ni content at the same Cu : Zn ratio increases stability of the beta phase at high temperatures suitable for hot extrusion, which can be reversed at intermediate annealing temperatures (~600°C). More particularly, an optical microscopy images of the as-cast structure is shown in Fig. 3a and the cold deformed annealed (450°C) is shown if Fig. 3b for alloy N° 3.

**[0045]** As described in the aforementioned invention of the first alloy the same low temperature heat treatment has been applied. According to the thermodynamic calculations shown in Figs. 4a and 4b the face-centered cubic (fcc) structure (alpha) is solidifying first followed by a body-centered-cubic phase (beta). At about 420°C the beta phase is partially transforming into a beta prime phase (b´), which is in accord with the microstructural observations of low temperature heat treatments (see Fig. 1 and Fig. 3b). The phase MnNi phase displayed in Figure 4 could not be manifested in the microstructure, due to too low reaction kinetics. The same is the case for low volume fraction phases thermodynamically stable at low temperatures, but due to low reaction kinetics not appearing. More particularly, Figs. 4a and 4b show pseudo-binary phase diagram (a) and phase fraction diagram for a specific composition (b) of alloy N° 3.

**[0046]** Said microstructure has been achieved with a Zn content of 38 and 39 wt.%. Lower Zn content lowers the amount of beta phase significantly, while Zn larger than 40 wt.% are showing a too low density of alpha grains.

**[0047]** Mechanical strength of this alloy reaches values between 850 – 1050 MPa and tensile elongations of 2 – 20 %. Such high strength values combined with good tensile elongations have not been reported so far to the knowledge of the inventors. One main key ingredient in achieving an optimum combination between strength and ductility is to perform two cycles of a low temperature heat treatment after significant cold deformation. This cyclic heat treatment allows for a maximum driving force to precipitate fine beta needles, at the expense of decreasing the dislocation density, which allows for further cold deformation. Meanwhile recrystallization and grain growth of alpha grains is kept to a minimum so that softening effects are avoided.

| Condition | Tensile tests | | |
|---|---|---|---|
| | Yield strength | Ultimate tensile strength | Total elongation |
| | [MPa] | | [%] |
| Composition A ; 450°C, 6h ; Ø 2.3 mm | 640 | 815 | 19 |
| Composition A ; 450°C, 6h ; + 350°C, 2h ; Ø 2.3 mm | 809 | 904 | 18.9 |
| Composition A ; 450°C, 6h ; Ø 1.6 mm | 687-702 | 891-898 | 12 |
| Composition A ; 450°C, 6h + 350°C, 2h ; Ø 1.6 mm | 724-809 | 848-904 | 8-19 |
| Composition B ; 350°C, 6h ; Ø 1.6 mm | 815-835 | 1020-1040 | 1 |
| Composition B ; 450°C, 6h + 350°C, 2h ; Ø 1.6 mm | 895-929 | 1000-1016 | 2-4 |

**Table 3.** Tensile test data for alloy N°:3

[0048] Fig. 5 shows screw-type and curly type chips shown for two types of alloys of the alloy N° 3.

[0049] Due to the uniform dispersion of softer and harder phases in the microstructure a good machinability (> 70% with respect to CuZn39Pb3 = 100%) is reached. Chip length is significantly longer than in the leaded alloys, however not affecting significantly the machining performance. Note that the surface quality is significantly better compared to the surface of the leaded alloy N°:1 (see Figure 6).

[0050] Figs. 6a to 6d represent machining tests with Mikron Multistar made at 100 Hz on alloy N°3 with composition A annealed at 450°C (Figs. 6a and 6b); and alloy N°:1 (Fig. 6c and 6d). Chip length of the leaded alloy N°:1 is smaller than that in alloy N°3.

[0051] Forth alloy

The forth alloy of the present invention is also unleaded and contains the following chemical composition: 45 – 48 wt.% Cu, 36 – 40 wt.% Zn, 9 – 14 wt.% Ni, 4 – 7 wt.% Mn, ≤ 0.5 wt.% Fe, ≤ 1.5 wt.% Ca, ≤1.0 wt.% Si, ≤1.0 wt.% Al, ≤0.03 wt.% P, ≤0.15 wt.% As and ≤0.1 wt.% Pb.

[0052] The main focus of this alloy was to introduce Ca into the material for it to act as a chip breaker when forming precipitates with Cu, Si, Al and Fe. In absence of Fe, Al and Si additions of Ca forms precipitates with Cu as has been demonstrated in the patent application WO2008/093974. Additions of at least one of the other alloying elements Si, Al or Fe further improve the machinability of this alloy.

[0053] The main difficulty with this type of alloy is the avoidance of oxidation of Ca as it strongly reacts with oxygen. This can be avoided by pre-alloying of Ca with Zn in inert atmosphere. Subsequent alloying with a pre-alloy of Cu-Mn incl. the above mentioned amounts of Fe, Si, Al.

**[0054]** Fifth alloy

The fifth alloy of the present invention can be unleaded and has the following chemical composition: 43.5 – 48 wt.% Cu, 36 – 40 wt.% Zn, 9 – 12 wt.% Ni, 5 – 7 wt.% Mn, ≤1.0 wt.% Al, ≤0.5 wt.% Sn, ≤0.5 wt.% Fe, ≤0.03 wt.% P, ≤ 0.15 wt.% As and ≤2.0 wt.% Pb.

**[0055]** The main focus of this alloy was to generate a variation of the aforementioned unleaded Cu-Ni-Zn-Mn alloy (Nº: 3) that is on the one hand age hardenable, i.e. forms secondary precipitates from a supersaturated solid solution matrix and on the other hand is suitable for hot and cold deformation, i.e. allows to be transformed from a duplex rich in beta structure into a duplex structure poor in the beta phase fraction. This was realized by including additions of Fe, Al and Sn.

**[0056]** Technically and economically speaking high beta phase fraction in the alloy during extrusion is beneficial as it allows for lowering the extrusion force and temperature. Subsequent cold drawing steps require however a high volume fraction of alpha grains, which if the chemistry is optimized can be achieved with dedicated heat treatment steps. This metallurgic ally difficult task has been fulfilled satisfactorily by the addition of Al and Sn.

**[0057]** The as-extruded microstructure shows a very fine recrystallized two-phased structure, with grain sizes well below 20 mm (Fig. 7a). Al acts in this respect as effective grain growth inhibitor. Subsequent heat treatments above 600°C exhibit some grain growth. Low temperature heat treatments exhibit a peak hardening at 350°C with Vickers hardness values of > 250 HV (see Table 4 and Figure 7).

**[0058]** Figs. 7a to 7d show as-extruded microstructure (Fig. 7a) and after 2 cycles of cold deformation and annealing at 650°C) (Fig. 7b) of alloy Nº 5. Heat treated alloy at 540°C followed by 350°C (Fig. 7c) and 400°C (Fig. 7d) low temperature heat treatment of alloy Nº 5.

**[0059]** Cycles of annealing (~600-700°C) and cold deformation treatments cause an alteration in the microstructure with an increasing content of the beta volume fraction to ~50%, whereby the alpha grains form the matrix surrounded by beta grains. When successively annealed at lower temperatures <450°C fine precipitates in form of needles nucleate (Fig. 7c and 7d).

**[0060]** According to thermodynamic simulations Ni-Aluminides are formed right after having reached the solidus curve and maintain a constant level of about 0.02 % and thus act as strong grain growth inhibitors as mentioned before. In addition Al has a strong effect on the variation of the beta fraction reaching a minimum value at around 600°C which towards higher and lower temperatures is increasing.

**[0061]** The tensile properties of the alloy show values ranging from 850 – 900 MPa with elongations of 2-12 % (see Table 4).

**[0062]** <u>Sixth alloy</u>
The sixth alloy of the present invention is also age hardenable and has the following chemical composition: 43.5 – 48 wt.% Cu, 36 – 40 wt.% Zn, 9 – 12 wt.% Ni, 5 – 7 wt.% Mn, ≤1.0 wt.% Al, ≤2.0 wt.% Sn, ≤0.5 wt.% Fe, Si ≤0.2 wt.%, ≤0.03 wt.% P, ≤ 0.15 wt.% As and ≤2 wt.% Pb.

**[0063]** The main focus of this alloy was to evaluate the influence Sn in the system, which has been added to provoke precipitation of NiSn phases.

**[0064]** A strong increase in the beta fraction with increasing Sn content has been observed, which allows for very low extrusion temperatures resulting in a high volume fraction of beta phase. Laboratory heat treatment and drawing tests have shown that this volume fraction can be decreased significantly allowing for subsequent good cold formability.

| Vickers hardness measurements for various combinations of heat treatments | | | | | |
|---|---|---|---|---|---|
| 500 / 4h | 540 / 4h | 560 / 4h | 580 / 4h | 600 / 4h | 640 / 4h |
| **175** | **171** | **171** | **157** | **157** | **146** |
| | | | | | |
| 500 / 4h | 540 / 4h | 560 / 4h | 580 / 4h | 600 / 4h | 640 / 4h |
| 300 / 8h | 300 / 8h | 300 / 8h | 300 / 8h | 300 / 8h | 300 / 8h |
| **232** | **232** | **227** | **227** | **241** | **234** |
| | | | | | |
| 500 / 4h | 540 / 4h | 560 / 4h | 580 / 4h | 600 / 4h | 640 / 4h |
| 350 / 8h | 350 / 8h | 350 / 8h | 350 / 8h | 350 / 8h | 350 / 8h |
| **252** | **244** | **237** | **206** | **221** | **234** |
| | | | | | |
| 500 / 4h | 540 / 4h | 560 / 4h | 580 / 4h | 600 / 4h | 640 / 4h |
| 400 / 8h | 400 / 8h | 400 / 8h | 400 / 8h | 400 / 8h | 400 / 8h |
| **223** | **206** | **221** | **214** | **225** | **212** |
| Tensile tests: | | | | | |
| Cold work reduction | Annealing temperature | Annealing time | Yield strength | Ultimate tensile strength | Total elongation |
| [%] | [°C] | [h] | [MPa] | [MPa] | [%] |
| 46 | 650 | 6 | 284 | 581 | 32.9 |
| 42.3 | 650 | 2 | 435 | 686 | 27.3 |
| 37.5 | 500 | 5 | 693 | 871 | 11.7 |
| 6 | 350 | 6 | 692 | 899 | 2.4 |

**Table 4:** Mechanical testing results of alloy N°:5.

**[0065]** Low temperature age hardening tests have shown a maximum hardening at ~350°C. The scanning electron microscopy (SEM) image shown in Fig.8 shows the material in the overaged condition heat treated at 400°C, where NiSn precipitates are visible as white dots in the beta phase and localized to the phase boundary.

**[0066]** Figs. 8a and b show optical microscopy image of a sample annealed at 540°C followed by a second annealing process at 400°C (Fig. 8a); Secondary electron microscopy image of alloy with NiSn preciptates in beta phase matrix and at boundary to alpha grains (Fig. 8b) both of alloy Nº: 6.

**[0067]** Vickers hardness measurements revealed a hardness of 230 – 240 HV for the age hardening at 350°C, while values between 220 – 230 HV were measured for heat treatments at 300 and 400°C comparable with values given in Table 4 for alloy N°:5, but slightly lower.

**[0068]** Seventh alloy

The seventh alloy of the present invention is also an age-hardenable alloy and has the following chemical composition: 43.5 – 48 wt.% Cu, 36 – 40 wt.% Zn, 9 – 12 wt.% Ni, 5 – 7 wt.% Mn, ≤0.1 wt.% Al, ≤0.1 wt.% Sn, ≤0.5 wt.% Fe, ≤1.0 wt .% Si, ≤0.3 wt.% P, ≤0.15 wt.% As and ≤2.0 wt.% Pb.

**[0069]** Again as the alloy inventions N$^{\underline{o}}$: 4 and 5, this invention aims for an age hardenable Cu-Ni-Zn-Mn alloy that apart from precipitations of alpha in beta or vice versa also contains typical alloying elements suitable for age hardenability. Here Silicon and Phosphorus are chosen as candidates.

**[0070]** Silicon has the strongest effect of all alloying elements on the alpha beta phase boundary in brasses and thus has to be added to the alloy with great care. Thermodynamic simulations have shown that additions of up to ~0.5 wt.% are still tolerable with respect to the balance of alpha/beta ratio (3:1, at 800°C), while a Si content of 1.0 wt.% reverses the fraction of alpha/beta completely for a Zn content of 37 wt.%.

**[0071]** Similar as the Ni-Aluminides precipitates in the previous mentioned alloy (N$^{\underline{o}}$: 5) here, Ni5Si2 precipitates are formed right after temperature has been lowered to below the solidus curve. However their detection is a non-trival task and was not successful with the instruments at hands. In low-alloyed copper the precipitates are nucleating and growing to rounded platelets [D. Zhao, Q.M. Dong, B.X. Kang, J.L. Huang, Z.H. Jin, Mater. Sci. Eng. A361, (2003). 93-99].

**[0072]** Additions of Phosphorous beyond the level used for de-oxidation is common in copper alloys containing either Fe or Ni. Such alloys are known for their excellent performance with respect to the combination of high conductivity paired with high strength. Typically they form small 20 - 50 nm sized circular particles of Fe2P [M. Motohisa, J. Jpn. Copper Brass Res.

Assoc. 29. (1990), 224-233; D.P. Lu, J. Wang, W.J. Zeng, Y. Liu, L.Lu, B.D. Sun, Mater. Sci. Eng. A421, (2006), 254-259] or hexagonal platelets, of NiP2 having sizes of 50-150 nm [J.S. Byun, J.H. Choi, D.N. Lee, Scripta Mater. 42, (2000), 637-643].

**[0073]** The age hardened stage of these alloys show a high mechanical resistance reaching hardness values beyond 250 HV and tensile strength above 1000 MPa with tensile elongation of 1 – 5 %.

## Claims

1. A precipitation hardenable copper alloy comprising, in percentage of weight, between 42 and 48 wt.% Cu, between 34 and 40 wt.% Zn, between 9 and 14 wt.% Ni, between 4 and 7 wt.% Mn, 2.0 wt.% or less of Pb, 1.0 wt.% or less of Al, 2.0 wt.% or less of Sn, 0.5 wt.% or less of Fe, 1.0 wt .% or less of Si, 1.5 wt.% or less of Ca, 0.15 wt.% or less of As, 0.3 wt.% or less of P, and unavoidable impurity elements such as: Mg, Cr, Cd, Co, S, Te, Zr,Sb and Ag amounting to less than 0.1 wt.%.

2. The copper alloy according to claim 1, further comprising 0.15 wt.% or less of As.

3. The copper alloy according to any of claims 1 or 2, having tensile strength values above 800 MPa and elongations above 5 % when subjected to a low temperature heat treatment comprised between about 300°C and about 450°C.

4. The copper alloy according to claim 3, wherein having a beta phase precipitated in a fine needle-like structure when subjected to the low temperature heat treatment.

5. The copper alloy according to claim 1, comprising between 45 and 48 wt.% Cu, between 37 and 40 wt.% Zn, between 9 and 14 wt.% Ni, between 4 and 7 wt.% Mn, 0.5 wt.% or less of Fe, 0.15 wt.% or less of As and 0.1 wt.% or less of Pb.

6. The copper alloy according to claim 5, having an alpha/beta structure with fine beta precipitates and having tensile strength greater than 880 MPa and elongations greater than 10 %, or having tensile strength of greater than 980 MPa and elongations greater than 2 %, and a machinability that is superior to the one of stainless steels, when subjected to a low temperature heat treatment comprised between about 300°C and about 450°C.

7. The copper alloy according to claim 1, comprising between 45 and 48 wt.% Cu, between 36 and 40 wt.% Zn, between 9 and 14 wt.% Ni, between 4 and 7 wt.% Mn, between 0.05 and 0.5 wt.% Fe, 1.5 wt.% or less of Ca, 1.0 wt .% or less of Si, 1.0 wt.% or less of Al, 0.15 wt.% or less of As, and 0.1 wt.% or less of Pb.

8. The copper alloy according to claim 7, wherein Ca forms precipitates with Cu and/or Zn in a pure alpha or a duplex alpha/beta structure.

9. The copper alloy according to claim 1, comprising between 43.5 and 48 wt.% Cu, between 36 and 40 wt.% Zn, between 9 and 12 wt.% Ni, between 5 and 7 wt.% Mn, 1.0 wt.% or less of Al, 0.5 wt.% or less of Sn, 0.5 wt.% or less of Fe, and 2.0 wt.% or less of Pb.

10. The copper alloy according to claim 9, wherein Al forms fine dispersed Ni-Aluminide particles/precipitates, yielding also a fine grained alpha/beta microstructure.

11. The copper alloy according to claim 1, comprising between 43.5 and 48 wt.% Cu, between 36 and 40 wt.% Zn, between 9 and 12 wt.% Ni, between 5 and 7 wt.% Mn, 1.0 wt.% or less of Al, 2.0 wt.% or less of Sn, between 0.05 and 0.5 wt.% Fe, 0.2 wt.% or less of Si, and 2 wt.% or less of Pb.

12. The copper alloy according to claim 11, wherein the presence of Al and Sn results in a high volume fraction of beta during a hot deformation, and which can be reduced during intermediate temperature annealing for allowing good cold formability, and NiSn-rich precipitates and or Ni-Al rich precipitates when submitted to a low temperature heat treatment comprised between about 300°C and about 450°C.

13. The copper alloy according to claim 1, comprising between 43.5 and 48 wt.% Cu, between 36 and 40 wt.% Zn, between 9 and 12 wt.% Ni, between 5 and 7 wt.% Mn, 0.1 wt.% or less of Al, 0.1 wt.% or less of Sn, 0.5 wt.% or less of Fe, 1.0 wt .% or less of Si, 0.3 wt.% or less of P, and 2.0 wt.% or less of Pb.

14. The copper alloy according to claim 13, wherein the presence of Si and P allows for the formation of either NiSi-rich precipitates or FeP /NiP precipitates when said alloy is subjected to an intermediate (350-550°C) temperature heat treatment.

15. The copper alloy according to any of the claims from 1 to 14, having hardness values comprised between 190 and 320 HV, tensile strength comprised between 550 and 700 MPa, and elongation greater than 25 % when the alloy is subjected to a high temperature heat treatment comprised between 500 and 700°C.

16. The copper alloy according to any of the claims from 1 to 15, having tensile strength greater than 800 MPa and tensile elongation greater than 5 % when the alloy is subjected to a low temperature heat treatment comprised between 300 and 450°C.

17. The copper alloy according to claim 1, having a microstructure containing fine-grained needle-like or globular-like precipitates of similar composition or different composition than the matrix and with grain size below 5 micron when the alloy is subjected to a low temperature heat treatment comprised between 300 and 450°C.

18. Copper alloy product, comprising the alloy according to any one of claims 1 to 17.

19. The copper alloy product according to claim 18, comprising wires, rods, strips, and rectangular shapes and profiles.

20. The copper alloy product according to claim 19, being obtained via casting, hot extrusion and successive cold drawing and heat treatment steps.

21. The copper alloy product according to the claims 19 or 20, wherein wires have a final diameter smaller than 2.5 mm.

22. The copper product according to claim 18, comprising a writing implement.

23. The copper product according to claim 22, wherein said writing implement comprises a pen tip, a tip socket and/or reservoir for pen tips to be filled with either oil-based, gel-based inks or other liquids.

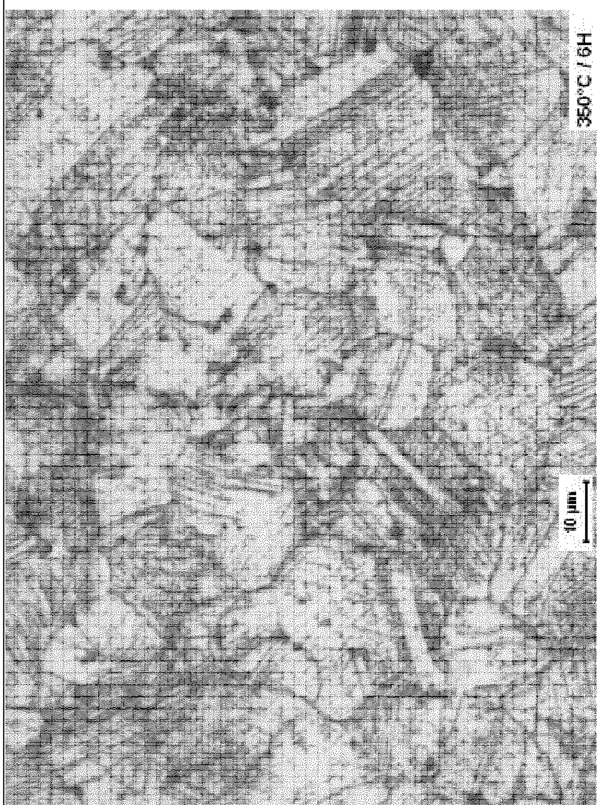


Fig. 1a

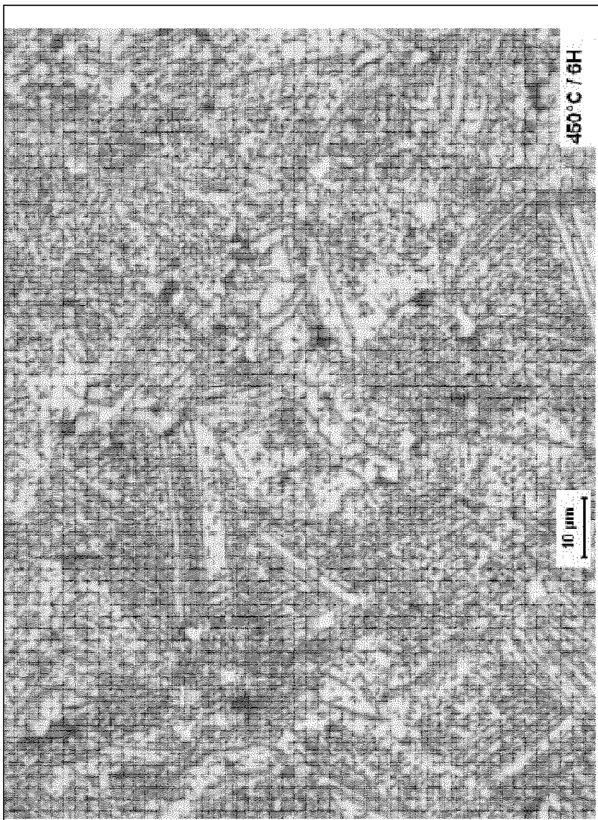


Fig. 1b

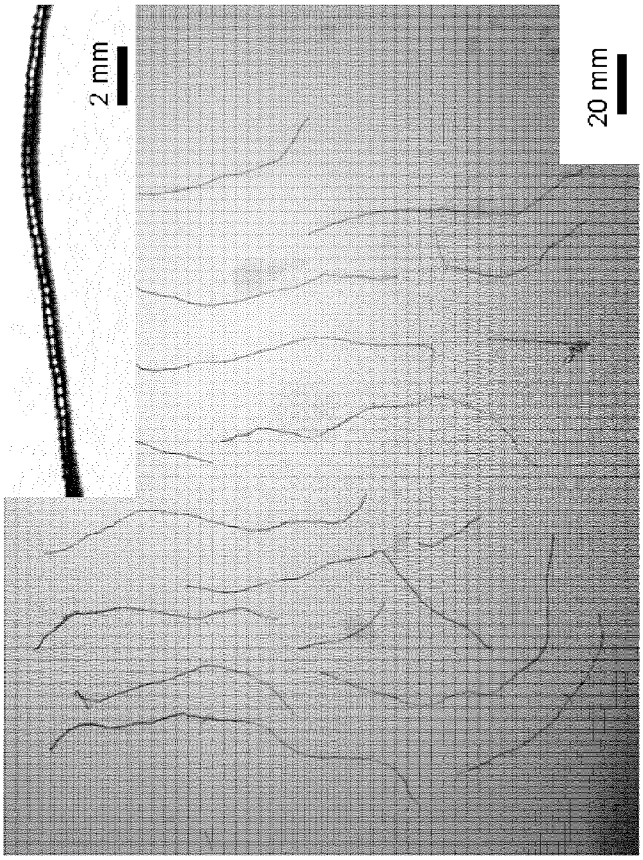


Fig. 2

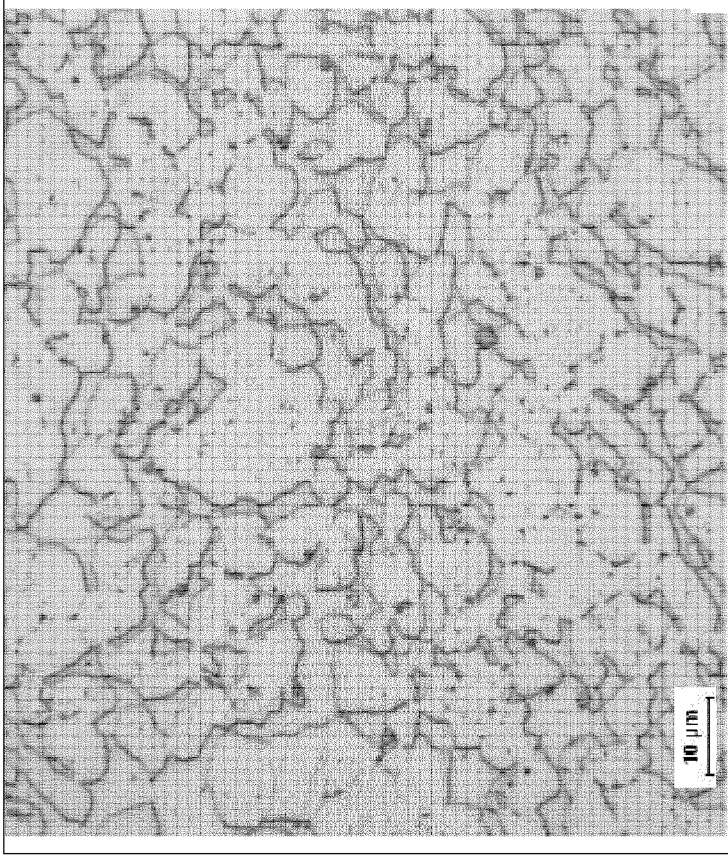


Fig. 3a

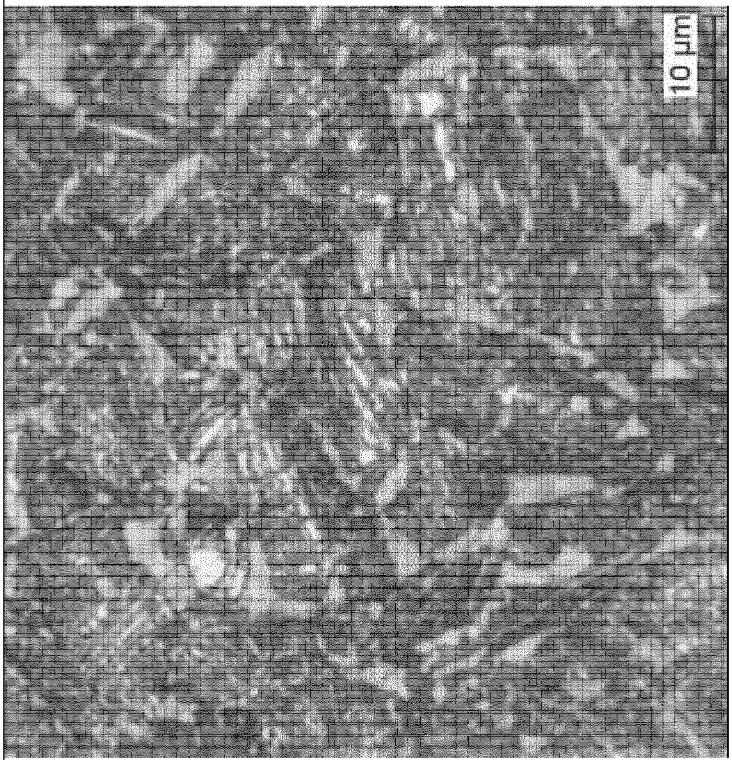


Fig. 3b

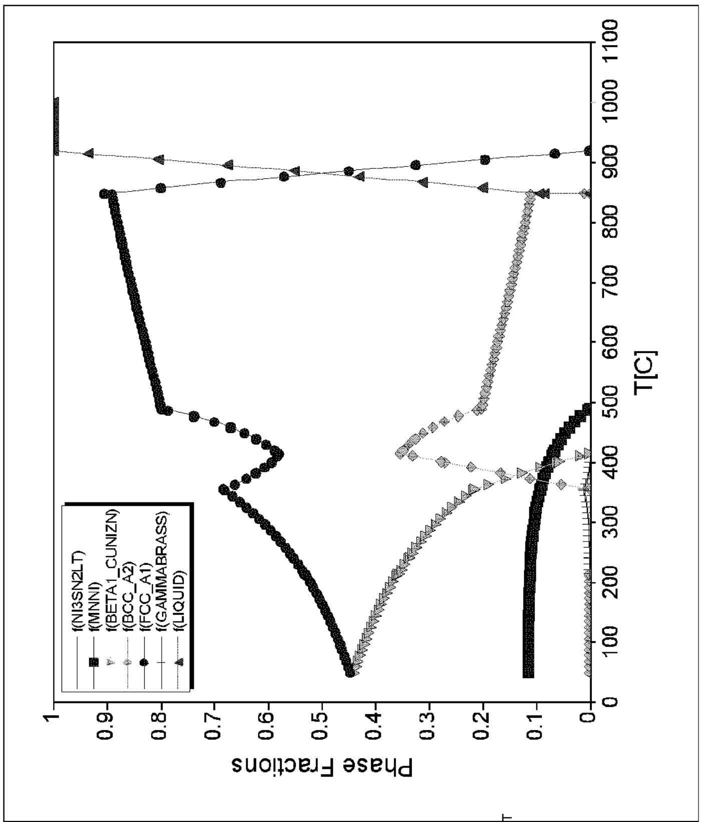
Phase Fractions
T[C]
f(NI3SN2LT)
f(MNNI)
f(BETA1_CUNIZN)
f(BCC_A2)
f(FCC_A1)
f(GAMMABRASS)
f(LIQUID)
0 100 200 300 400 500 600 700 800 900 1000 1100
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

Fig. 4b

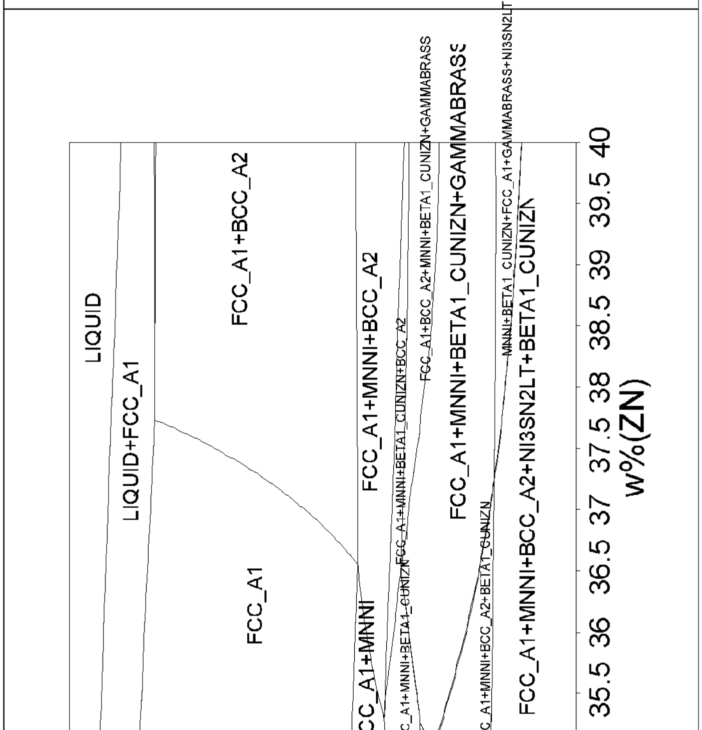
T[C]
w%(ZN)
100 200 300 400 500 600 700 800 900 1000
35 35.5 36 36.5 37 37.5 38 38.5 39 39.5 40
LIQUID
LIQUID+FCC_A1
FCC_A1
FCC_A1+BCC_A2
FCC_A1+MNNI
FCC_A1+MNNI+BCC_A2
FCC_A1+MNNI+BETA1_CUNIZN+GAMMABRASS
FCC_A1+MNNI+BCC_A2+NI3SN2LT+BETA1_CUNIZN

Fig. 4a

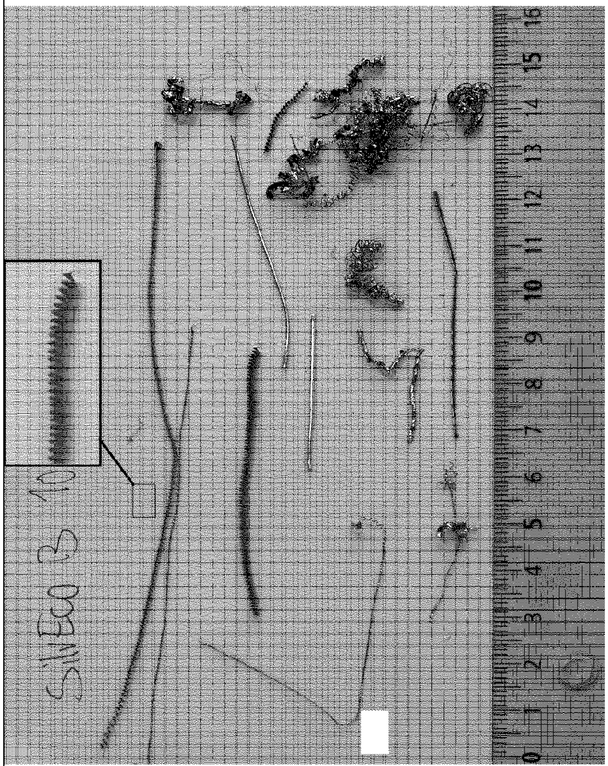

Fig. 5b

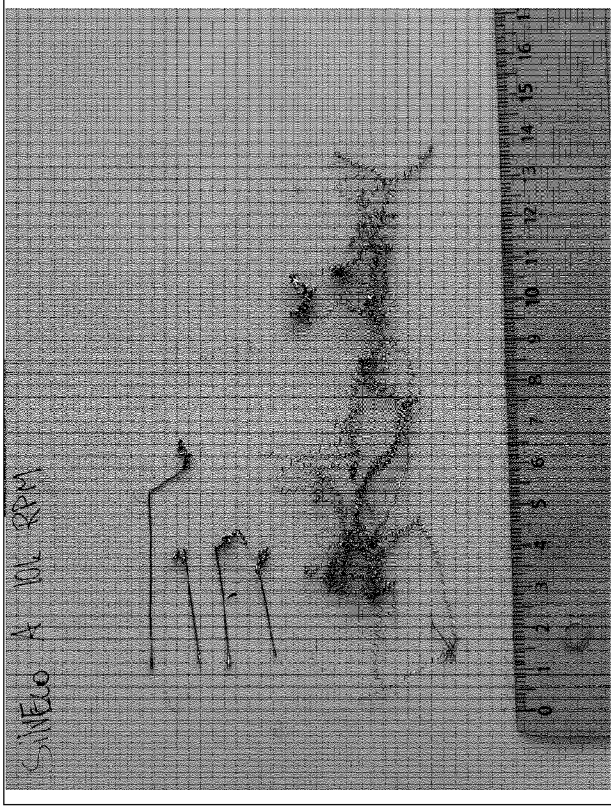

Fig. 5a

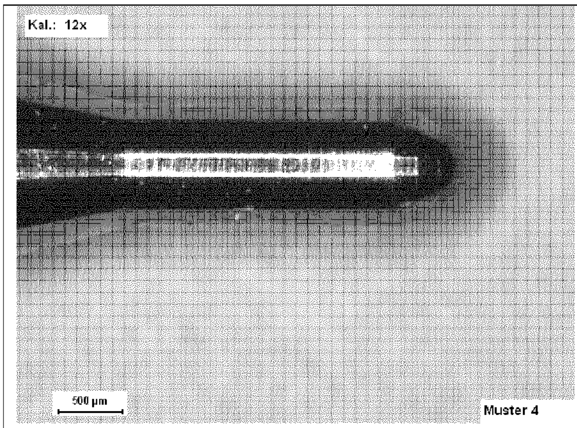


Fig. 6a

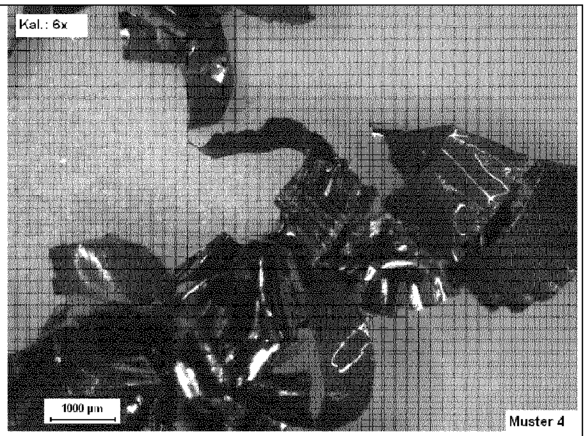


Fig. 6b

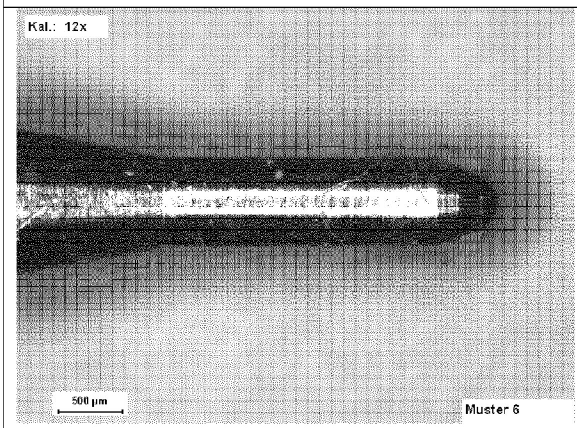


Fig. 6c

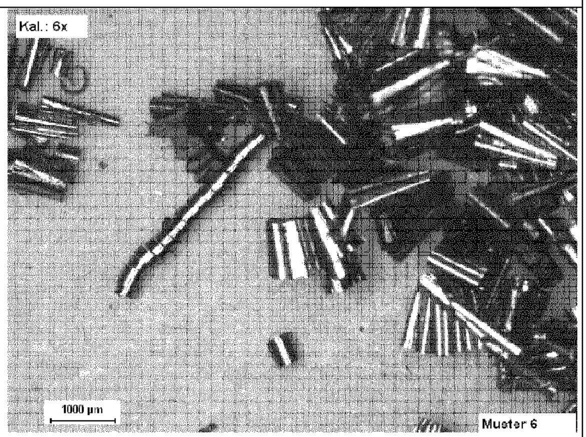


Fig. 6d

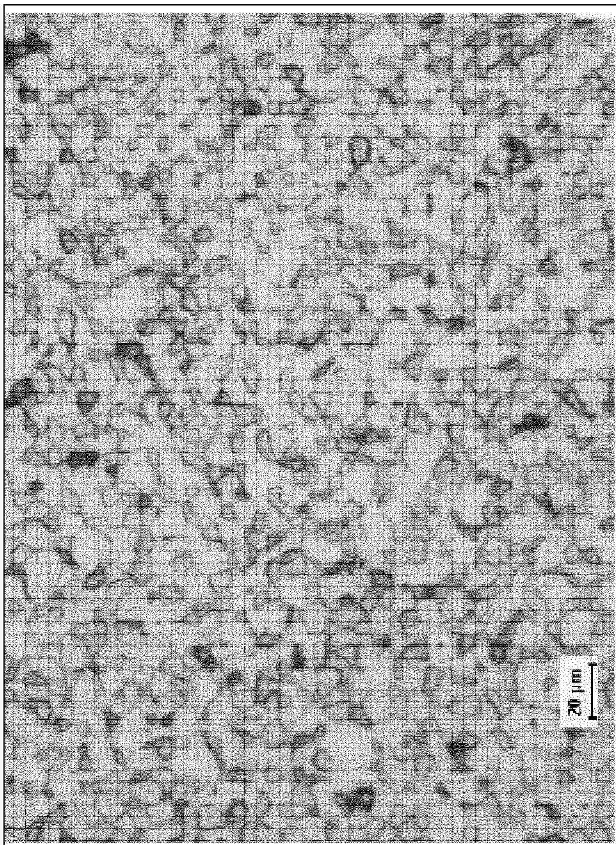


Fig. 7b

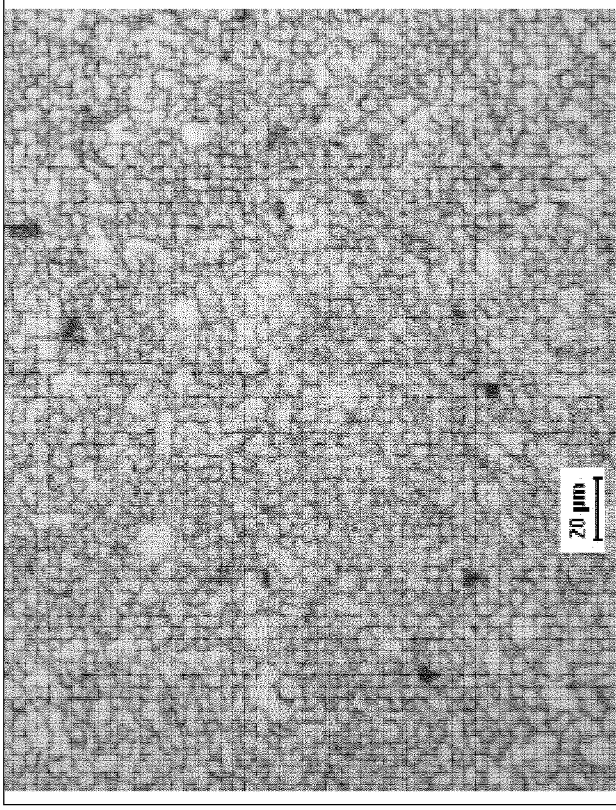


Fig. 7a

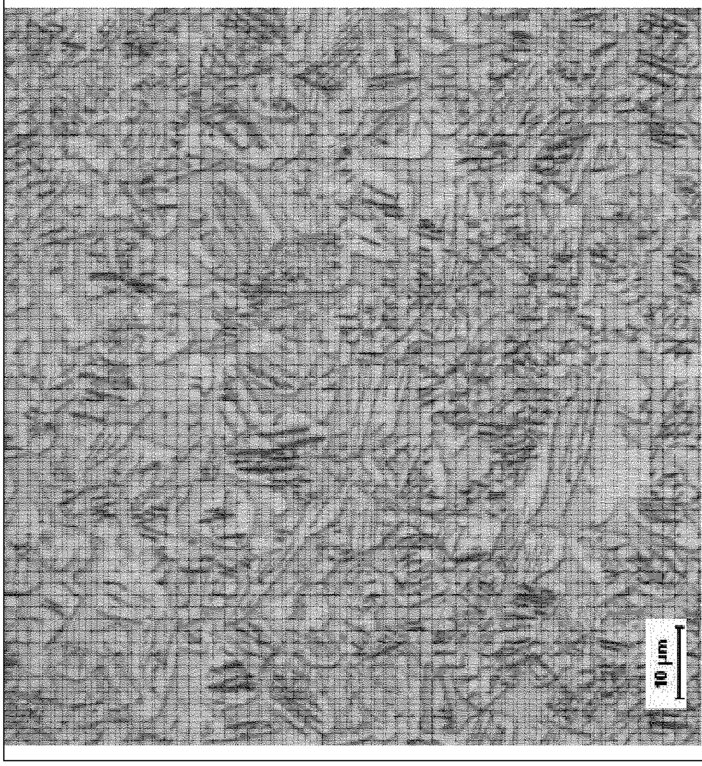


Fig. 7c

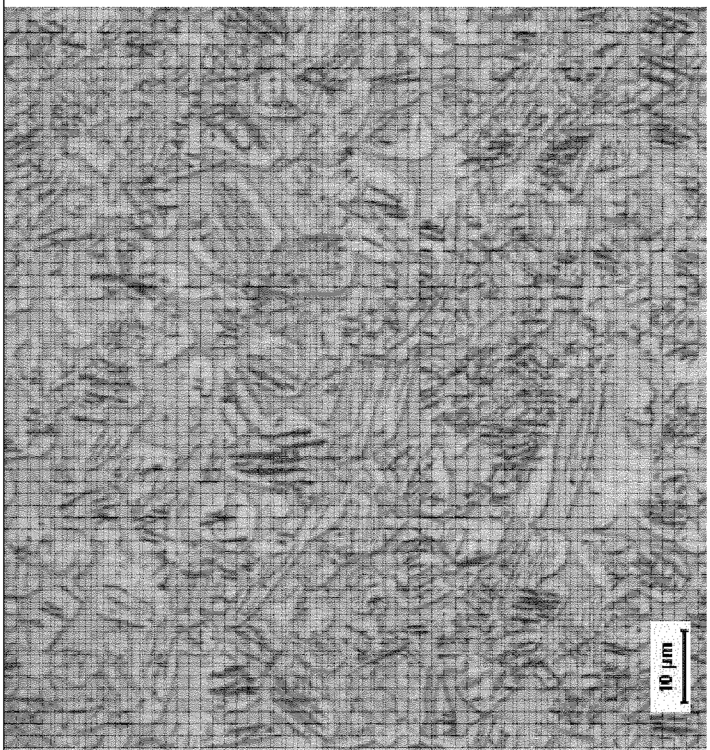


Fig. 7d

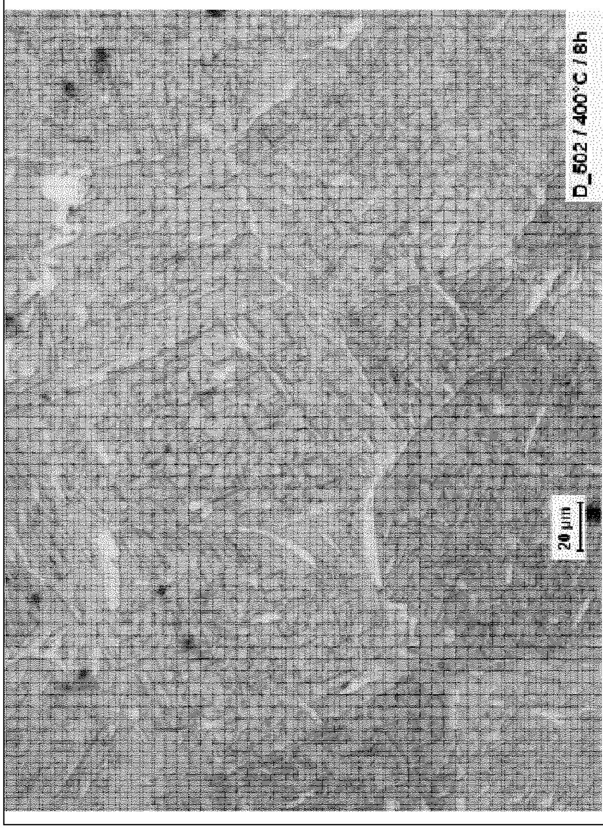
D_502 / 400°C / 8h
20 µm

Fig. 8a

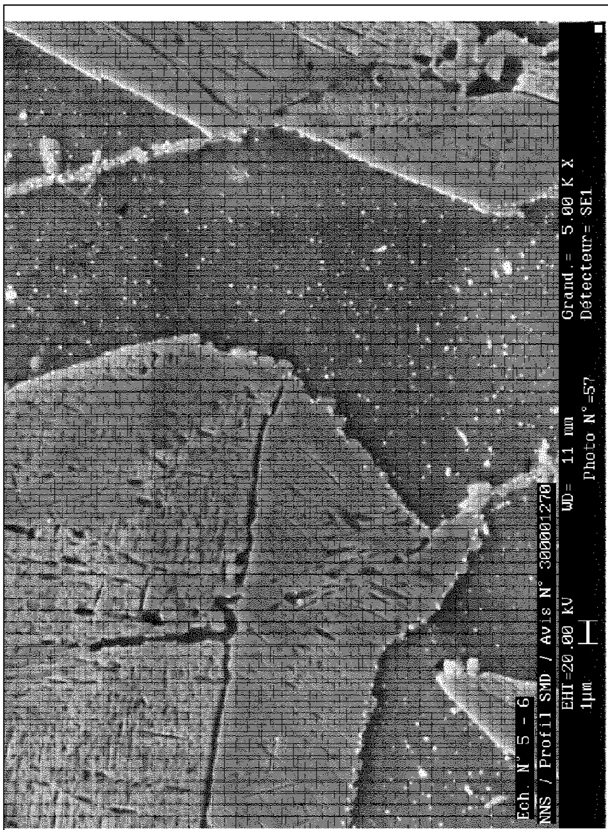
Ech. N° 5 - 6
NNS / Profil SMD / Avis N° 3000012708
EHT=20.00 kV WD= 11 mm Grand.= 5.00 K X
1µm Photo N°=57 Détecteur= SE1

Fig. 8b