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

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

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

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 Nº 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

[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 Nº 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,

[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.

Claims

1. A precipitation hardenable copper alloy consisting of, in percentage of weight, 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, 2.0 wt.% or less of Pb, 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, 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.%, wherein
the copper alloy is configured to have tensile strength values above 800 MPa and elongations above 5 % by low temperature heating the alloy between 300°C and 450°C.

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

3. The copper alloy according to claim 1 or 2, wherein
having a beta phase precipitated in a fine needle-like structure when subjected to the low temperature heat treatment.

4. 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.

5. The copper alloy according to claim 4, wherein
Ca forms precipitates with Cu and/or Zn in a pure alpha or a duplex alpha/beta structure.

6. The copper alloy according to claim 1, 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 300°C and 450°C.

7. The copper alloy according to any of the claims from 1 to 6, 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.

8. The copper alloy according to any of the claims from 1 to 7, 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.

9. 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.

10. Copper alloy product, comprising the alloy according to any one of claims 1 to 9.

11. The copper alloy product according to claim 10, comprising wires, rods, strips, and rectangular shapes and profiles.

12. The copper alloy product according to claim 10, being obtained via casting, hot extrusion and successive cold drawing and heat treatment steps.

13. The copper alloy product according to the claims 10 or 11, wherein wires have a final diameter smaller than 2.5 mm.

14. The copper product according to claim 10, comprising a writing implement.

15. The copper product according to claim 14, 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.

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, Electrochimica 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 high strength, good corrosion resistance and improved machinability in combination 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

range that allows to vary the microstructure (fraction of beta content) from 0% to approximately 50% ± 10%. Zn content > 40 wt.% show a too 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] First alloy:
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

optimization of thermo-mechanical treatment as it was done for unleaded alloys (see further down).

[0034] 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 Nº 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, Electrochimica 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

[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 alloy, 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 in Fig. 3b for alloy Nº 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 (β′), which is in accord with the microstructural observations of low temperature heat treatments (see Fig. 1 and Fig. 3b). The 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,

[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, addition 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 µm (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 an as-extruded microstructure (Fig. 7a), after 2 cycles of cold deformation and annealing at 650°C) (Fig. 7b), heat treated at 540°C followed by 350°C (Fig. 7c), and 400°C low temperature heat treatment (Fig. 7d) of alloy Nº 5.

Claims

1. A precipitation hardenable copper alloy consisting of, in percentage of weight, 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, 2.0 wt.% or less of Pb, 1.0 wt.% or less of Al, 2.0 wt.% or less of Sn, between 0.05 and 0.5 wt.% of Fe, 0.2 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.%; wherein the copper alloy is configured to have tensile strength values above 800 MPa and elongations above 5 % by low temperature heating the alloy between 300°C and 450°C.

2. The copper alloy according to claim 1, wherein having a beta phase precipitated in a fine needle-like structure when subjected to the low temperature heat treatment.

3. The copper alloy according to claim 1, wherein Ca forms precipitates with Cu and/or Zn in a pure alpha or a duplex alpha/beta structure.

4. The copper alloy according to claim 1, 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.

5. The copper alloy according to claim 1, 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.

6. The copper alloy according to claim 1, 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.

7. 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.

8. Copper alloy product, comprising, in percentage of weight, between 43.5and 48 wt.% Cu, between 36 and 40 wt.% Zn, between 9 and 12 wt.% Ni, between 5 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, between 0.05 and 0.5 wt.% of Fe, 0.2 wt.% or less of Si..

9. The copper alloy product according to claim 8, comprising wires, rods, strips, and rectangular shapes and profiles.

10. The copper alloy product according to claim 8, being obtained via casting, hot extrusion and successive cold drawing and heat treatment steps.

11. The copper alloy product according to claim 8, wherein wires have a final diameter smaller than 2.5 mm.

12. The copper product according to claim 8, comprising a writing implement.

13. The copper product according to claim 12, 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.