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(54) **Titre : ALLIAGE CUIVRE-ZINC-SILICIUM, SON UTILISATION ET SA PRODUCTION**
(54) **Title: COPPER/ZINC/SILICON ALLOY, USE AND PRODUCTION THEREOF**

(57) **Abrégé/Abstract:**
The invention relates to a Cu-Zn-Si alloy comprising 70-80 wt. % copper, 1 -5 wt. % silicon, 0.0001 0.5 % boron, up to 0.2 % phosphorus and/or up to 0.2 % arsenic, the rest being zinc in addition to unavoidable impurities. The information further relates to the use and production of said alloy. The alloy is characterized by improved resistance to oxidation and by uniform mechanical properties.

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Abstract

The invention relates to a Cu-Zn-Si alloy comprising, in % by weight, 70 to 80% of copper, 1 to 5% of silicon, 0.0001 to 0.5% of boron, up to 0.2% of phosphorus and/or up to 0.2% of arsenic, remainder zinc plus inevitable impurities, and to the use and production of an alloy of this type, the alloy being distinguished by an improved resistance to oxidation and by uniform mechanical properties.

Copper/zinc/silicon alloy, use and production thereof

The invention relates to a copper-zinc-silicon alloy and to the use and production of a copper-zinc-silicon alloy of this type.

A priority requirement of copper-zinc-silicon alloys is that they be resistant to dezincification and machineable. Hitherto, good machining properties of brass alloys of this type has been realized by the addition of lead, as described, for example, in EP 1 045 041 A1. Recently, however, lead-free brass alloys with good machining properties have been developed, as described, for example, in EP 1 038 981 A1 and DE 103 08 778 B3. Both lead-free and lead-containing Cu-Zn-Si alloys have a tendency to be oxidized and form a layer of scale at temperatures between 300°C and 800°C. This layer of scale is only loosely bonded to the metal and can easily become detached from it, so that it is then dispersed through the production facilities, with the result that this layer has a disruptive contaminating effect. The production facilities are expensive to clean, making production costs high. A further drawback of the known Cu-Zn-Si alloys is that the mechanical properties of the material change over long workpieces, since the material lacks homogeneity.

In view of these facts, the present invention is therefore based on the problem of providing a copper-zinc-silicon alloy which is improved in terms of its homogeneity and, furthermore, is less prone to the formation of scale, and to provide the use and production of a brass alloy of this type.

The first aspect, relating to an alloy, is achieved according to the invention by a copper-zinc-silicon alloy comprising, in % by weight, 70 to 80% of copper, 1 to 5% of silicon, 0.0001 to 0.5% of boron, 0 to 0.2% of phosphorus and/or arsenic, remainder zinc plus inevitable impurities.

In one embodiment of the first aspect, the invention relates to a Cu-Zn-Si alloy, comprising, in % by weight: 70 to 80% of copper; 1 to 5% of silicon; 0.0001 to 0.004% of boron; at least one of: 0 to 0.5% of gold, 0 to 0.3% of cadmium, 0 to 0.3% of selenium, 0 to 0.3% of tellurium, 0 to 0.3% of bismuth, 0 to 0.2% arsenic; 0 to 0.2% of phosphorus; and remainder zinc plus inevitable impurities.

In a further embodiment of the first aspect, the invention relates to a Cu-Zn-Si alloy, comprising, in % by weight: 70 to 80% of copper; 1 to 5% of silicon; 0.0001 to 0.0004% of boron; 0 to 0.2% of phosphorus; and remainder zinc plus inevitable impurities.

The copper content is between 70 and 80%, since copper contents of below 70% or above 80% would have an adverse effect on the machining properties of the alloy. The same applies if the silicon concentration departs from the indicated range of 1% to 5%. The boron concentration in the alloy is between 0.0001 and 0.5%. Surprisingly, it has now been found that the addition of boron within the concentration range claimed on the one hand reduces the formation of scale and on the other hand significantly improves the bonding of the remaining scale to the material. Furthermore, it is also surprising that the addition of boron improves the homogeneity of the microstructure and thereby prevents fluctuations in the mechanical properties. Phosphorus and arsenic may each be present in the alloy in a concentration of up to 0.2%, and can be substituted for one another. Phosphorus and arsenic have a beneficial effect on the formation of the initial cast microstructure and the corrosion properties, and furthermore improve the flow properties of the melt and reduce the susceptibility to stress corrosion cracking. The remaining main component of the alloy is zinc.

In addition to the advantages listed above of avoiding easily detached layers of scale which increase production costs and improving the mechanical properties and, furthermore, good machining properties and shaping properties in combination with a high resistance to corrosion are provided, the resistance to dezincification and stress corrosion cracking are also particularly pronounced in the invention. Dezincification tests carried out in accordance with ISO 6509 give dezincification depths of only up to 26 μm.

The second aspect, relating to the use of a copper-zinc-silicon alloy of this type, is achieved by its use for electrical engineering components, for sanitaryware components, for vessels for transporting or storing liquids or gases, for torsionally loaded components, for recyclable components, for drop-forged components, for semi-finished products, for strips, for sheets, for profiled sections, for plates or as a wrought, rolled or cast alloy.

The Cu-Zn-Si alloy is used for contacts, pins or securing elements in electrical engineering, for example as stationary contacts or fixed contacts, including clamping and plug connections or plug-in contacts.

The alloy has a high resistance to corrosion with respect to liquid and gaseous media. Moreover, it is extremely resistant to dezincification and stress corrosion cracking. Consequently, the alloy is particularly suitable for use for vessels for transporting or storing liquids or gases, in particular for vessels used in refrigeration or for pipes, water fittings, valve extensions, pipe connectors and valves in sanitaryware.

The low corrosion rates also ensure that the metal leaching, i.e. the property of losing alloying constituents through the action of liquid or gaseous media, is inherently low. In this respect, the material is suitable for application areas which require low pollutant emissions in order to protect the environment. Therefore, the alloy according to the invention can be used in the field of recyclable components.

The lack of susceptibility to stress corrosion cracking means that the alloy is recommended for use in screwed or clamped connections in which for technical reasons high elastic energies are stored. Therefore, the alloy is particularly suitable for all components which are subject to tensile and/or torsional loads, in particular for nuts and bolts. After cold-forming, the material achieves high values for the proof stress. Consequently, greater tightening torques can be realized in screw connections which must not be plastically deformed. The yield strength ratio of the Cu-Zn-Si alloy is lower than in the case of free-machining brass. Screw connections which are tightened only once and in the process are deliberately over-extended therefore achieve particularly high holding forces.

Possible uses of the Cu-Zn-Si alloy result for starting materials in both tube and strip form. The alloy is also eminently suitable for strips, sheets and plates which can be milled or punched, in particular for keys, engravings, for decorative purposes or for leadframe applications.

The third aspect relating to production of a copper-zinc-silicon alloy of this type is achieved by conventional continuous casting and hot-rolling at between 600 and 760°C with subsequent deformation, in particular cold-rolling, preferably with the addition of further annealing and deformation steps.

The aspect relating to production of a copper-zinc-silicon alloy of this type is also achieved by conventional continuous casting and extrusion at up to 760°C, preferably between 650 and 680°C, followed by cooling in air.

In an advantageous refinement of the Cu-Zn-Si alloy, the alloy comprises 75 to 77% of copper, 2.8 to 4% of silicon and 0.001 to 0.1% of boron, as well as 0.03 to 0.1% of phosphorus and/or arsenic, as well as zinc as remainder element plus inevitable impurities.

In a preferred alternative, the copper-zinc-silicon alloy comprises at least one element, in % by weight, selected from the group consisting of 0.01 to 2.5% of lead, 0.01 to 2% of tin, 0.01 to 0.3% of iron, 0.01 to 0.3% of cobalt, 0.01 to 0.3% of nickel and 0.01 to 0.3% of manganese. The addition of lead has a positive influence on the machining properties.

The alloy in this case advantageously comprises at least one element, in % by weight, selected from the group consisting of 0.01 to 0.1% of lead, 0.01 to 0.2% of tin, 0.01 to 0.1% of iron, 0.01 to 0.1% of cobalt, 0.01 to 0.1% of nickel and 0.01 to 0.1% of manganese.

In a preferred refinement, the Cu-Zn-Si alloy in addition comprises at least one element, in % by weight, out of up to 0.5% of silver, up to 0.5% of aluminium, up to 0.5% of magnesium, up to 0.5% of antimony, up to 0.5% of titanium and up to 0.5% of zirconium, and preferably selected from the group consisting of 0.01 to 0.1% of silver, 0.01 to 0.1% of aluminium, 0.01 to 0.1% of magnesium, 0.01 to 0.1% of antimony, 0.01 to 0.1% of titanium and 0.01 to 0.1% of zirconium.

In an advantageous alternative, the Cu-Zn-Si alloy in addition comprises at least one element, in % by weight, selected from the group consisting of up to 0.3% of cadmium, up to 0.3% of chromium, up to 0.3% of selenium, up to 0.3% of tellurium and up to 0.3% of bismuth, preferably selected from the group consisting of 0.01-0.3% of cadmium, 0.01-0.3% of chromium, 0.01-0.3% of selenium, 0.01-0.3% of tellurium and 0.01-0.3% of bismuth.

An exemplary embodiment is explained in more detail with reference to the drawing and with reference to the following description. In the drawing:

Fig. 1 shows the formation of a layer of scale after annealing for 2 h at 600°C on a CuZn21Si3P alloy without the addition of boron (a), a CuZn21Si3P alloy containing 0.0004% of boron (b), and a CuZn21Si3P alloy containing 0.009% of boron (c), and

Fig. 2 shows the formation of the cast microstructure of a CuZn21Si3P alloy without the addition of boron (a), a CuZn21Si3P alloy with 0.0004% of boron (b), and of a CuZn21Si3P alloy containing 0.009% of boron (c).

The CuZn21Si3P alloys on which the exemplary embodiment is based have variations in concentration of the components, with copper amounting to between 75.8 and 76.1%, silicon amounting to between 3.2 and 3.4% and phosphorus amounting to between 0.07 and 0.1%, together with zinc as the remainder plus inevitable impurities. The alloy examples have different boron contents, at 0%, 0.004% and 0.009%. The alloys are produced by continuous casting followed by extrusion at temperatures below 760°C, preferably between 650 and 680°C, followed by rapid cooling.

All the alloys have an excellent resistance to dezincification. A dezincification test carried out in accordance with ISO 6509 reveals dezincification depths of only less than 26 µm.

If CuZn21Si3P alloys are exposed to temperatures of 300-800°C, for example during hot-working, scale is formed, and this scale can easily become detached and contaminate the production facilities. An extensively scaled surface of a boron-free CuZn21Si3P alloy is illustrated in Fig. 1a. The surface of the specimen appears predominantly grey in Fig. 1a. This grey colour reveals the scaled surface of the CuZn21Si3P alloy. Only a few individual bright spots without any regular distribution are visible on the surface of the alloy. By contrast, the CuZn21Si3P alloy with a boron content of 0.0004% in Fig. 1b has a very much greater number of white spots on the surface of the alloy than the boron-free alloy. These white spots represent bright metallic regions of the alloy. These bright metallic regions, i.e. regions without any scale, are distributed uniformly over the surface of the alloy. The proportion of the surface on which scale has formed is considerably reduced and the remaining scale is more securely bonded to the metal than in the case of the boron-free alloy. Fig. 1c illustrates a CuZn21Si3P alloy containing 0.009% of boron. This figure clearly reveals that the number of bright metallic surfaces, i.e. of white spots, has increased further. In some areas, there are relatively large continuous regions of bright metallic material, and the figure also reveals a very regular distribution on the surface of the alloy. The proportion of the surface on which scale has formed has decreased further, and the remaining scale is securely bonded to the metal. Therefore, it has surprisingly emerged that low boron concentrations of 0.0001 - 0.5% restrict the formation of scale on Cu-Zn-Si alloys and at the same time considerably increase the bonding of the scale to the metal, with the result that undesirable contamination of the production facilities is avoided.

A similar result was also found for Cu-Zn-Si-P alloys with different lead content, such as for example 0.01%, 0.05%, 0.1% or 2.5%.

In addition to reducing the susceptibility to scaling of Cu-Zn-Si alloys, boron also has a positive effect on the mechanical properties, since boron makes the microstructure of the alloy more homogeneous. This change to the microstructure of the alloy is illustrated in Fig. 2 as a function of the boron concentrations. Whereas a CuZn21Si3P alloy without the addition of boron has a coarse, inhomogeneous microstructure (Fig. 2a), a CuZn21Si3P alloy containing 0.0004% of boron has a significantly more homogeneous microstructure which already has very uniform grain sizes (Fig. 2b). A further increase in the boron content to 0.009% results in an even more uniform CuZn21Si3P alloy of even greater homogeneity, in which the grains of the microstructure can no longer be seen by the naked eye (Fig. 2c).

In addition to optical changes to the microstructure, the addition of boron also has beneficial effects on the mechanical properties. This is particularly apparent on rods which have been extruded from Cu-Zn-Si alloys. To determine the mechanical properties, samples were taken at the start and end of such rods. The tensile strength of a rod made from a CuZn21Si3P alloy without the addition of boron differs by more than

60 N/mm^2 at the start of the rod compared to the end of the rod. A corresponding alloy with a boron content of 0.0004%, by contrast, has a tensile strength difference of only less than 40 N/mm^2 between the start and end of the rod. If 0.009% of boron is added to a CuZn21Si3P alloy, the difference in the tensile strength between the start and end of the rod is less than 5 N/mm^2.

Therefore, the material has identical mechanical properties throughout. Accordingly, a uniform strength is achieved over the entire extruded length. The reason for this is the grain-refining action of boron.

The table reveals the relationship between the boron content of a Cu-Zn-Si alloy and the increasing homogeneity of the alloy microstructure or the decreasing strength differences within an extruded workpiece.

Alloy	Position	Tensile strength in N/mm^2
CuZn21Si3P	Start of extrusion	514
	End of extrusion	578
CuZn21Si3P containing 0.0004% of boron	Start of extrusion	507
	End of extrusion	545
CuZn21Si3P containing 0.009% of boron	Start of extrusion	508
	End of extrusion	512

CLAIMS:

1. A Cu-Zn-Si alloy, comprising, in % by weight:

70 to 80% of copper;

1 to 5% of silicon;

0.0001 to 0.004% of boron;

at least one of:

0 to 0.5% of gold,

0 to 0.3% of cadmium,

0 to 0.3% of selenium,

0 to 0.3% of tellurium,

0 to 0.3% of bismuth;

0 to 0.2% arsenic;

0 to 0.2% of phosphorus; and

remainder zinc plus inevitable impurities.

2. The Cu-Zn-Si alloy according to claim 1, comprising, in % by weight, at least one of:

0.01 to 0.1% of gold,

0.01 to 0.3% of cadmium,

0.01 to 0.3% of selenium,

0.01 to 0.3% of tellurium, and

0.01 to 0.3% of bismuth.

3. A Cu-Zn-Si alloy, comprising, in % by weight:

70 to 80% of copper;

1 to 5% of silicon;

0.0001 to 0.0004% of boron;

0 to 0.2% of phosphorus; and

remainder zinc plus inevitable impurities.

4. The Cu-Zn-Si alloy according to claim 1 or 2, comprising, in % by weight:

75 to 77% of copper;

2.8 to 4% of silicon;

0.0001 to 0.004% of boron;

0.03 to 0.1% of phosphorus; and

0.03 to 0.1% of arsenic.

5. The Cu-Zn-Si alloy according to any one of claims 1 to 4, comprising, in addition, at least one element, in % by weight, selected from the group consisting of:

0.01 to 2.5% of lead;

0.01 to 2% of tin;

0.01 to 0.3% of iron;

0.01 to 0.3% of cobalt;

0.01 to 0.3% of nickel; and

0.01 to 0.3% of manganese.

6. The Cu-Zn-Si alloy according to claim 5, comprising, in addition, at least one element, in % by weight, selected from the group consisting of:

0.01 to 0.1% of lead;

0.01 to 0.2% of tin;

0.01 to 0.1% of iron;

0.01 to 0.1% of cobalt;

0.01 to 0.1% of nickel; and

0.01 to 0.1% of manganese.

7. The Cu-Zn-Si alloy according to any one of claims 1 to 4, comprising, in addition, at least one element, in % by weight, selected from the group consisting of:

0 to 0.5% of silver;

0 to 0.5% of aluminium;

0 to 0.5% of magnesium;

0 to 0.5% of antimony;

0 to 0.5% of titanium; and

0 to 0.5% of zirconium.

8. The Cu-Zn-Si alloy according to claim 7, comprising, in addition, at least one element, in % by weight, selected from the group consisting of:

0.01 to 0.1% of silver;

0.01 to 0.1% of aluminium;

0.01 to 0.1% of magnesium;

0.01 to 0.1% of antimony;

0.01 to 0.1% of titanium; and

0.01 to 0.1% of zirconium.

9. The Cu-Zn-Si alloy according to any one of claims 1 to 8, comprising, in addition, in % by weight, greater than 0 to 0.3% of chromium.

10. The Cu-Zn-Si alloy according to claim 9, comprising, in addition, in % by weight, 0.01 to 0.3% of chromium.

11. Use of the Cu-Zn-Si alloy according to any one of claims 1 to 10, for: an electrical engineering component, a sanitaryware component, a vessel for transporting or storing a liquid or gas, a torsionally loaded component, a recyclable component, a drop-forged component, a semi-finished product, a strip, a sheet or a profiled section, a plate; or as a wrought, rolled or cast alloy.

12. A process for producing the Cu-Zn-Si alloy according to any one of claims 1 to 10, by continuous casting and hot-rolling at between 600 and 760°C with subsequent deformation.

13. The process according to claim 12, wherein the subsequent deformation is by cold-rolling.

14. The process according to claim 12 or 13, wherein the subsequent deformation is with the addition of further annealing and deformation steps.

15. A process for producing a Cu-Zn-Si alloy according to any one of claims 1 to 10, by continuous casting and extrusion at up to 760°C, followed by cooling in air.

16. The process according to claim 15, wherein the continuous casting and extrusion is at between 650 and 680°C.

Application number / numéro de demande: EP05/05238

Figures: Fig1 A,B,C Fig2 A,B,C

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