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(72) **Inventeur/Inventor:**
HANSEN, ANDREAS, DE

(73) **Propriétaire/Owner:**
GEBR. KEMPER GMBH + CO. KG METALLWERKE, DE

(74) **Agent:** RICHES, MCKENZIE & HERBERT LLP

(54) **Titre :** PIECES FORMEES FAITES D`UN ALLIAGE DE CUIVRE USINABLE ET RESISTANT A LA CORROSION
(54) **Title:** SHAPED PARTS MADE OF A CORROSION-RESISTANT AND MACHINABLE COPPER ALLOY

(57) **Abrégé/Abstract:**
The present invention concerns a copper alloy, its use and a process for the inanufacture of mouldings, and the mouldings made therefrom. The alloy comprises by weight %:
Sn: 2 to 6%
Zn: 0.1 to 5%
S: 0.1 to 0.45 %
Pb: less than 0,25
Ni: less than 0.6
Sb: less than 0,2
and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu.

ABSTRACT

The present invention concerns a copper alloy, its use and a process for the manufacture of mouldings, and the mouldings made therefrom. The alloy comprises by weight %:

Sn: 2 to 6%

Zn: 0.1 to 5%

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SHAPED PARTS MADE OF A CORROSION-RESISTANT AND MACHINABLE COPPER ALLOY

[0001] This invention concerns a copper alloy, its use and a process for the production of mouldings, as well as the mouldings made from it.

State of the art

[0002] Water is a valuable raw material and indispensable for daily use. Therefore, when drinking water is taken from the supply system, it has to be microbiologically so that its subsequent consumption does not lead to any human illness. In order to achieve this, high demands are placed on materials that come into direct contact with drinking water. Copper is the noblest commodity material and is regarded as an indispensable material in industry and technology for water-bearing systems. Copper has bacteriostatic properties and also offers excellent corrosion resistance. Copper also shows positive properties in shaping. Copper casting alloys are easy to cast and the high strength and toughness of the material also make it particularly suitable for plastomechanical forming.

[0003] However, it is precisely this plastic deformability that causes problems during machining. Here, homogeneous copper materials tend to form long chips. This type of chip inhibits the work sequence during fully automatic turning or drilling and leads to heavy wear on the tool cutting edges. The chip formation of copper is often the limiting factor in mechanical machining and therefore has a direct influence on the economic efficiency of the workpieces.

[0004] Gunmetal belongs to the group of copper casting alloys and is characterised by the combination of good castability with optimum machinability and high strength. Due to its good corrosion resistance, gunmetal is particularly suitable for water-bearing systems such as fittings and sanitary technology. Common gunmetal alloys contain tin to increase strength and corrosion resistance. Zinc is added as a cost-effective substitute for copper. In order to be able to process the products made of gunmetal economically at all, the heavy metal lead is added, which acts as a chip breaker in the alloy and makes machining possible on CNC machines and conventional automatic lathes.

[0005] If the drinking water stagnates over a longer period of time in commercially available lead-containing fittings, there is a possibility that lead may be released into the tap water through metal ion migration. High lead concentrations are considered harmful to health. For this reason, ever stricter requirements are being imposed worldwide on the lead content of materials that come into contact with drinking water. Within Germany, too, the lead content has been reduced to 10 µg lead/l since 01.12.2013 via the statutory drinking water ordinance. The pressure to further reduce lead content in drinking water has increased worldwide and will continue to grow. For example, legal requirements from the USA require that lead contents in copper alloys must not exceed an average lead content of 0.25 %, irrespective of the actual lead concentration in drinking water.

[0006] The ideal gunmetal would be free of lead and other questionable substances, with the same or better efficiency in production and without impairing corrosion resistance, high mechanical strength and good processability.

[0007] EP 2290114 A1 describes a lead-free gunmetal alloy with 4 to 6 wt.% tin, 4 to 6 wt.% zinc and less than 0.25 wt.% lead. With this alloy, lead-free components can be produced by means of casting processes. However, the subsequent mechanical processing to create the functional surfaces of these components is not taken into account. Without lead, the specified composition shows a homogeneous α-MK microstructure which tends to form long chips and cannot be machined economically. The presupposed casting process also requires a higher material input for the production of the moulded part than alternative forming processes. The US 2012/0082588 A1, the EP 2 241 643 A1, the EP 3 225 707 A1 and the US 9,181,606 B2 reveal copper alloys.

EP 2 872 660 B1 describes a forming process for a lead-free gunmetal alloy. A process for preconditioning a gunmetal alloy containing 2 to 8% by weight tin, 2.5 to 13% by weight zinc and less than 0.25% by weight lead which is suitable for hot pressing and exhibits a homogeneous structure at the end of the hot pressing process is described. Hot forming enables the economical production of shaped parts with low material input. Although the process sequence up to the shaping of the blank is explained, the subsequent machining process necessary for the elaboration of functional surfaces of the components is not taken into account. Due to the chemical composition and the subsequent hot forming, a homogeneous microstructure is created and here, too, the absence of a chip breaker can be expected to result in long chip formation during machining, which makes economic machining of the components more difficult.

[0009] EP 1 801 250 A1 describes low-migration components made of a copper alloy with a relatively high content of Si, in addition to lower but significant proportions of Mn, Al and Zr. Similar copper alloys are also disclosed in WO 2007/068470.

[0010] Despite the many copper alloys now known in the state of the art, it is still a challenge to specify gunmetal copper alloys which, on the one hand, manage without the use of lead (Pb), which is problematic from an environmental and health point of view, and, on the other hand, enable forming processes without impairing the mechanical properties and corrosion resistance. The provision of copper alloys which show good hot formability (i.e. without any significant drop in mechanical properties) and are also preferably easy to machine has proved to be particularly challenging.

Task of the present invention

[0011] Due to the above-mentioned disadvantages in the state of the art, it is the task of the present invention to indicate a copper alloy which overcomes these disadvantages. In particular, a copper alloy that comprises as few components as possible, is lead-free or essentially lead-free and can also dispense with expensive metal components and/or metal components that are difficult to mix in would be desirable.

Short description of the invention

[0012] This task is solved by the copper alloy, its use, and the process for the production of moulded parts having features described herein. Preferred designs are indicated in the following description. The moulded parts manufactured using the copper alloy described here are also subject to stress.

Accordingly, in one aspect the present invention resides in a copper alloy for use in the manufacture of shaped parts by a process comprising at least one hot forming operation, the alloy having the following composition in % by weight:

Sn: 2 to 6%, preferably 2 to 4%
Zn: 0.1 to 5%, preferably 0.1 to 3%
S: 0.05 to 0.45%, preferably 0.1 to 0.45 %
Pb: less than 0,25
Ni: less than 0.6
Sb: less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu.

In another aspect, the present invention resides in use of a copper alloy for the manufacture of shaped parts by a process comprising at least one hot forming operation, the alloy having the following composition in % by weight:

Sn: 2 to 6%, preferably 2 to 4%
Zn: 0.1 to 5%, preferably 0.1 to 3%
S: 0.05 to 0.45%, preferably 0.1 to 0.45 %
Pb: less than 0,25
Ni: less than 0.6
Sb: less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu.

In a further aspect, the present invention resides in a process for the production of shaped parts from a copper alloy, wherein the alloy has the following composition in % by weight:

Sn: 2 to 6%, preferably 2 to 4%
Zn: 0.1 to 5%, preferably 0.1 to 3%
S: 0.05 to 0.45%, preferably 0.1 to 0.45 %
Pb: less than 0,25
Ni: less than 0.6
Sb: less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu; said process comprising the steps of: at least one hot forming operation of the copper alloy to produce a shaped article.

More preferably, in the copper alloy the sum of the impurities does not exceed 0.25 % by weight.

Detailed description of the invention

[0013] The present invention is described in the following first of all with regard to the alloy in accordance with the invention. However, it is clear to the skilled person that the preferred designs described in this context can also be applied to the described use, the described manufacturing process and the described moulded parts and must also be regarded as preferred designs for these aspects of the invention.

[0014] This invention makes it possible to produce shaped parts with high mechanical strength, high dimensional stability and high corrosion resistance from a gunmetal alloy, which has a chip breaker in its microstructure, by means of hot forming with low material input. These parts can then also be subjected to economic machining after hot pressing. The hot-formable gunmetal alloy of the present invention does not require elements such as Al, Si, Pb, Sb, Te, Se, C and Bi to form a chip breaker in the microstructure and is therefore easily reusable.

[0015] The present invention thus provides a copper alloy which has the following composition in % by weight, in particular for the production of shaped parts from at least one hot forming process followed by machining:

Sn: 2 to 6%

Zn: 0 to 5%

S: 0.05 to 0.6 %

Pb: less than 0,25

Ni: less than 0.6

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Sb: less than 0,2 %,

optionally further containing phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.003% by weight, Zr to a maximum of 0.03% by weight and unavoidable impurities, the sum of the impurities preferably not exceeding 0.25% by weight, and the remainder being Cu.

[0016] As stated above, in particular, the alloy invented does not contain elements of the group Al, Si, Sb, Te, Se, C and Bi and, in preferred forms, does not contain Pb either.

[0017] Preferred contents of alloy components to be used in accordance with the invention are as follows, whereby these are disclosed and claimed individually as well as in each combination in accordance with the invention (in each case again in % by weight):

Sn: 2 to 4 %, in embodiments 2 to less than 3.5 %, such as 2 to 3.25

Zn: 0 to 3 %, in embodiments 0 to less than 1,5 %, in particular 0,1 to less than 1,5 %

S: 0.1 to 0.45% and, in embodiments, 0.1 to less than 0.25%, such as 0.1 to 0.2%.

Ni: less than 0.5%, such as from 0 to 0.4%, from 0 to 0.25%

[0018] The copper content in the alloy is preferably 88 wt.% or more, more preferably 90 wt.% or more.

[0019] It has been shown unexpectedly that the copper alloys disclosed here can overcome the known disadvantages from the state of the art. In particular, semi-finished and intermediate products made of copper alloys can be subjected to hot forming very well. Despite the frequent degradation of strain hardenings during hot forming (typically at temperatures of about 600 to 950°C), the alloy according to the invention makes it possible to produce shaped parts (which may then be further processed, e.g. by machining) which still have excellent mechanical properties and do not show any degradation of corrosion resistance.

[0020] Furthermore, it has been shown that the formed parts obtained in this way (i.e. after hot forming) can also be further processed in an economical manner, since in particular the undesired formation of long chips is avoided. It can thus be seen that, despite the processes involved in hot forming, chip breaking components are still present in the microstructure of the alloy, although the alloy according to the invention dispenses with typical chip breaking components such as Pb or Si. So the invention at hand provides a copper alloy with an excellent balance of desired properties. It is therefore possible to produce shaped parts from this alloy, in particular by hot forming, possibly combined with further processing steps as described here, without having to fear any reductions in the other desired properties of the copper alloy and its suitability for use in hot forming.

[0021] The alloy in accordance with the invention can thus be used advantageously for the manufacture of shaped parts, whereby these manufacturing processes include hot forming, possibly combined with other machining processes, such as subsequent machining.

In order to maintain the desired properties of the copper alloy described here, the individual alloy components alone and in their interaction allow good and reproducible control of the alloy properties.

[0022] Tin acts in the alloy as a solid solution hardener and thus increases tensile strength, yield strength and hardness, but reduces elongation at break. Furthermore, tin increases the corrosion resistance, whereby the corrosion resistance increases with increasing tin contents. During the production of the blanks for hot forming it could be recognized that strong segregations occur in the microstructure due to tin, which lead to the formation of zone crystals during solidification. At the beginning of solidification, copper crystals with a lower tin content are precipitated and the residual melt is enriched with a tin content that is higher than the average content of the alloy. Deviating from the stable copper-tin state diagram, a eutectoid may be present in the microstructure at room temperature at contents of more than 7 wt.% tin ($\alpha + \delta$); under equilibrium conditions, this eutectoid is only formed at max. 15.8 wt.% tin. The possible δ phase crystallizes in the kfz lattice and should therefore be easily deformable, but the phase has a brittle behavior due to its voluminous elementary cell of 416 atoms. This makes the subsequent hot forming process more difficult. The eutectoid can be removed by heat treatment at high temperatures with sufficient time ($\alpha + \delta$), but heat treatment requires a lot of energy.

[0023] There is also a risk of grain enlargement of the microstructure during treatment. This would lead to a reduction in elongation, making the subsequent hot forming process more difficult. With a content of 2 to 6 wt.% tin, especially preferred 2 - 4 wt.% tin, a high mechanical strength with high elongation is guaranteed and the formation of eutectoid ($\alpha + \delta$) in the cast state is avoided.

[0024] Sulphur is almost insoluble in solid copper and the original properties of the material, such as corrosion resistance, are not affected by the addition of sulphur. Due to its insolubility in solid copper, sulphur leads to a constitutive behaviour that influences the solidification process of copper-tin alloys in a similar way to lead. Unlike lead, however, at the end of solidification sulphur is not present in the microstructure as an element, but in the form of an intermetallic metal-sulphur compound which is evenly distributed in the microstructure. It could be recognized that this phase is incoherent and brittle in the microstructure and thus generates a chip breaking mechanism.

[0025] The properties of the sulphides influence the mechanical, plastic behaviour of the gunmetal material. The influence is determined by the amount of sulfide phases in the material. From sulphur contents above 0.6 % by weight, the stress transmitting α-Cu matrix is so strongly affected by the sulphides that a hot pressing process is very difficult. The sulphur content of 0.05 wt.% to 0.6 wt.%, particularly preferably 0.1 wt.% to 0.45 wt.%, ensures that sufficient sulphide inclusions are present in the microstructure to produce a chip breaking mechanism and ensure a hot forming process.

[0026] Zinc is added to the alloy as an economic substitute for copper. It has been recognised that there is a close relationship between the zinc content and the sulphur content over the time and the type of distribution of sulphide formation. The higher the zinc content, the earlier the sulphide inclusions form in the microstructure during casting solidification. If the zinc content is above 5% by weight, the sulphide formation is shifted to temperatures in the range of the solidification temperature of the gunmetal alloy. In this temperature range there are still high molten parts in the casting structure which are connected to each other in places.

[0027] A high zinc content then leads to early formation of the sulphides. These sulfides are inhomogeneous and concentrated in the microstructure and thus make the hot pressing process more difficult due to a local weakening of the α-MK matrix. If the zinc content is low, the formation is shifted to lower temperatures and the sulphides are present in former residual melt areas separately from each other and homogeneously distributed. The zinc content of 0 to 5 % by weight, particularly 0 to 3 % by weight zinc, ensures that sulphide formation at higher temperatures is avoided.

Investigations have shown that the copper alloy according to the invention has a special suitability for use in a manufacturing process for shaped parts due to its specific composition, which process comprises at least one hot forming. Due to the special composition of the alloy, further processing steps can be carried out after hot forming without any problems, for example subsequent machining.

[0029] A hot forming process in accordance with the invention can, for example, be a hot pressing process. According to the invention, however, other hot forming processes are also possible which are known to the specialist. The blank is heated to 600 °C to 950 °C before hot forming, for example a hot pressing process. From 600 °C, the yield strength is sufficiently low to plastically deform the gunmetal material using a hot forming process. According to the invention, hot forming can be carried out at any suitable temperature within the above temperature window, for example 700 to 900°C. The respective temperature is selected by the specialist depending on the type of moulded part, the desired speed of forming, etc.

[0030] It was recognized that in the given temperature range also the atomic bonds of the sulfides become weaker, so that dislocation movements in these superstructures are facilitated. In this temperature range, the phases lose their brittleness and become deformable and thus do not inhibit the hot forming process. Immediately after forming, a dynamic recrystallization of the α-MK matrix takes place, which removes the previously cast zone solid solution with different tin concentrations and ensures a homogeneous concentration across the cross-section and thus constant mechanical characteristics and corrosion properties.

[0031] After the deformation process at room temperature, however, the sulphides are distributed again in the microstructure and are brittle, so that they act as chip breakers. It was possible to determine that even with thermoformed moulded parts with low sulphur contents of 0.05 wt.% or more, jerking of the tool occurs during mechanical machining due to temporally changed friction between chip and tool. These changed friction conditions are due to the inhomogeneous microstructure which, after the hot pressing process, consists of a copper-containing α-MK matrix with sulphides embedded in it. Shear bands are produced in the chip due to the jerky sliding, which lead to lamellar chips and shear chips and break in the further course of the machining process when discharged via a chip guide step in the tool. This prevents long chips and enables economical machining.

[0032] In order to enable the hot pressing process envisaged in the invention, the average grain size in the cast state should not exceed 2 mm. The necessary measures to ensure such an average grain size are known to the expert. Grain refinement is possible, for example, by using chemical additives such as zirconium and boron up to contents of 0.005 to 0.03% by weight or other alternative processes to grain refinement such as electromagnetic stirring, ultrasonic excitation, vibration, gas injection or by means of strong subcooling of the melt during casting.

[0033] The copper alloy described above is particularly suitable for use in the manufacture of shaped parts, the manufacture comprising at least one hot forming operation. It can also be used for the production of shaped parts, in which at least one hot forming operation is followed by further processing steps, such as subsequent machining. The corresponding manufacturing process is particularly suitable for the manufacture of components, e.g. media pipes, e.g. gas or water pipes, and components to be connected, e.g. fittings, etc. Fittings that are particularly in focus are components of domestic plumbing pipe systems, including pipes, fittings, end caps and connectors. The basic process steps for the manufacture of such moulded parts are known to the specialist and will therefore not be described in detail here.

In this context, it is essential to note that the specific composition of the copper alloy to be used, as described above, means that there is no drop in mechanical properties and corrosion resistance even after hot forming. In addition, it has been shown that both before and after hot forming, the parts obtained can be subjected to other machining processes without any problems. In particular, machining is possible as the problematic and undesirable formation of long chips is avoided. In this way, a moulded part can be produced in an economic manner (in particular since the other desirable properties of the copper alloy, such as good hot working properties, inertness to substances in contact with the parts, in particular drinking water, and corrosion resistance, are not affected). In this context, it should be particularly emphasized that the advantages of this invention described here are achieved, although the use of the components Pb, Si etc., which are otherwise often considered necessary in the state of the art, is dispensed with.

[0033] This unexpected advantage of the copper alloy described here enables its economic use in the manufacture of the moulded parts described above.

Example

[0034] From a lead-free gunmetal, a shaped part for the drinking water installation was produced in a fine grain state by means of hot forming with subsequent machining. This showed that after the hot pressing process chip breakers were present in the microstructure of the alloy, so that economic fully automated mechanical processing was possible.

We claim:

1. Copper alloy for use in the manufacture of shaped parts by a process comprising at least one hot forming operation, the alloy having the following composition in % by weight:

Sn: 2 to 4%

Zn: 0.1 to 3%

S: 0.05 to 0.45 %

Pb: less than 0,25

Ni: less than 0.6

Sb: less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu.

2. The copper alloy according to claim 1, wherein the sum of said impurities does not exceed 0.25% by weight.

3. The copper alloy, according to claim 1 or claim 2, wherein the alloy is free of the elements selected from the group consisting of Al, Si, Sb, Te, Se, C and Bi and/or wherein the alloy is free of Pb.

4. The copper alloy, according to any one of claims 1 to 3 wherein the copper alloy is for use in producing shaped parts by a process further comprising machining after the at least one hot forming, the process further comprising the step of machining after the at least one hot forming; or wherein the use comprises machining following the hot forming.

5. A shaped article made of the copper alloy according to any one of claims 1 to 4.

6. Use of a copper alloy for the manufacture of shaped parts by a process comprising at least one hot forming operation, the alloy having the following composition in % by weight:

Sn :	2 to 4%
Zn:	0.1 to 3%
S:	0.05 to 0.45 %
Pb:	less than 0,25
Ni:	less than 0.6
Sb :	less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu.

7. The use according to claim 6, wherein the sum of said impurities does not exceed 0.25% by weight.

8. The use according to claim 6 or claim 7, wherein the alloy is free of the elements selected from the group consisting of Al, Si, Sb, Te, Se, C and Bi and/or wherein the alloy is free of Pb.

9. The use according to any one of claims 6 to 8, wherein the copper alloy is for use in producing shaped parts by a process further comprising machining after the at least one hot forming, the process further comprising the step of machining after the at least one hot forming; or wherein the use comprises machining following the hot forming.

10. A shaped article made of the copper alloy obtained by the use according to any of claims 6 to 9.

11. Process for the production of shaped parts from a copper alloy, wherein the alloy has the following composition in % by weight:

Sn: 2 to 4%

Zn: 0.1 to 3%

S: 0.05 to 0.45%

Pb: less than 0,25

Ni: less than 0.6

Sb: less than 0,2

and optionally phosphorus to a maximum of 0.06% by weight, B to a maximum of 0.03% by weight, Zr to a maximum of 0.03% by weight, and unavoidable impurities, and the balance being Cu; said process comprising the steps of:

at least one hot forming operation of the copper alloy to produce a shaped article.

12. The process as claimed in claim 11, wherein the sum of said impurities does not exceed 0.25% by weight.

13. The process as claimed in claim 11 or claim 12, wherein the alloy is free of the elements selected from the group consisting of Al, Si, Sb, Te, Se, C and Bi and/or wherein the alloy is free of Pb.

14. The process as claimed in any one of claims 11 to 13, wherein the copper alloy is for se in producing shaped parts by a process further comprising machining after the at least one hot forming, the process further comprising the step of machining after the at least one hot forming; or wherein the use comprises machining following the hot forming.

15. A shaped article made of the copper alloy obtained by the process according to any one of claims 11 to 14.