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CA 2635470 C 2017/03/28

(11)(21) **2 635 470**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(22) **Date de dépôt/Filing Date:** 2008/06/20
(41) **Mise à la disp. pub./Open to Public Insp.:** 2008/12/28
(45) **Date de délivrance/Issue Date:** 2017/03/28
(30) **Priorité/Priority:** 2007/06/28 (DE102007029991.7-24)

(51) **Cl.Int./Int.Cl.** *C22C 9/04* (2006.01), *B21C 37/06* (2006.01), *F16C 33/12* (2006.01)

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(54) **Titre :** ALLIAGE DE CUIVRE ET DE ZINC, PROCEDE DE FABRICATION ET UTILISATION
(54) **Title:** COPPER-ZINC ALLOY, PRODUCTION METHOD AND USE

(57) **Abrégé/Abstract:**

The invention relates to a copper-zinc alloy,
consisting of (in wt%):
from 28.0 to 36.0% Zn,
from 0.5 to 2.3% Si,
from 1.5 to 2.5% Mn,
from 0.2 to 3.0% Ni,
from 0.5 to 1.5% Al,
from 0.1 to 1.0% Fe,
optionally also up to at most 0.1% Pb,
optionally also up to at most 0.2% Sn,
optionally also up to at most 0.1% P,
optionally also up to 0.08% S,
remainder Cu and inevitable impurities, with mixed silicides of iron-nickel-manganese incorporated in the matrix.

05869P0163CA01

Abstract

Copper-zinc alloy, production method and use

The invention relates to a copper-zinc alloy, consisting of (in wt%):

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from 0.5 to 2.3% Si,
from 1.5 to 2.5% Mn,
from 0.2 to 3.0% Ni,
from 0.5 to 1.5% Al,
from 0.1 to 1.0% Fe,
optionally also up to at most 0.1% Pb,
optionally also up to at most 0.2% Sn,
optionally also up to at most 0.1% P,
optionally also up to 0.08% S,
remainder Cu and inevitable impurities, with mixed silicides of iron-nickel-manganese incorporated in the matrix.

Copper-zinc alloy, production method and use

Description

The invention relates to a copper-zinc alloy, to methods for producing tubes or rods from the copper-zinc alloy and to its use.

Owing to the greatly increasing stress on materials for friction bearings and the rising operating pressures and temperatures in modern machines, engines and equipment, the demands on the properties of the alloys suitable for use are increasing.

For this reason there is a need to further develop the operating properties of materials for bearings. This entails on the one hand increasing the strength properties, the heat resistance of the structure and the complex wear resistance while simultaneously having sufficient ductility properties. On the other hand, the friction bearing alloy must have a sufficient performance in the event of lubrication supply failure, which avoids seizure of the bearing partners. To date, copper alloys containing lead have been used for this purpose.

Documents DE 10 2004 058 318 B4 and DE 10 2005 015 467 A1 disclose the application possibilities of a copper-zinc alloy for use as a valve guide and friction bearing with high thermal and wear stability. The alloy consists of 59 - 73 wt% copper, 2.7 - 8.5 wt% manganese, 1.5 - 6.3 wt% aluminum, 0.2 - 4 wt% silicon, 0.2 - 3 wt% iron, 0 - 2 wt% lead, 0 - 2 wt% nickel, 0 - 0.4 wt% tin and the remainder zinc.

Increasing the thermal and wear stability for these alloys with an extremely high alloy content of manganese and aluminum generally entails a β-matrix, in which α-precipitates and hard phases are incorporated. Although the wear and heat resistance of these alloys may be regarded as sufficient, this unilateral orientation of the structural adjustment detrimentally affects the ductility properties of the material.

Furthermore, DE 29 19 478 C2 discloses the use of a similar alloy for synchronous rings. In respect of this use, it is regarded as advantageous that there is an improved wear-resistance and at the same time a significantly increased coefficient of friction. The semifinished products made from the alloy furthermore have good processability; they can readily be cold-formed owing to the relatively high aluminum content, although an increase in hardness at room temperature is to be noted compared with the previously conventional special brasses. The aluminum content lies in the range of from 4 to 6 wt%.

The further document US Patent No. 3,773,504 discloses a copper-based alloy which is wear-resistant at high temperature for a valve seat in combustion engines, which likewise has a comparatively high aluminum content of from 5 to 12 wt%. The aluminum content in the specified range improves the corrosion resistance in addition to the effect of reinforcing the matrix.

A further increase in the wear resistance occurs through the formation of an intermetallic phase of manganese and silicon.

The patent application published for opposition DE 1 194 592 discloses a method for producing synchronous rings, which are distinguished by a high and constant coefficient of friction, a high wear resistance and good machining processability. To this end annealing treatments of the alloy, consisting substantially of β-phase at between 200 and 500°C, are proposed in order to achieve from 5 to 50% α-precipitation.

A certain lead content is usually provided in said documents for better machining processability.

It is an object of the invention to provide a copper-zinc alloy having improved cold formability, higher hardness and heat resistance.

In one aspect of the invention there is provided a copper-zinc alloy, consisting of, in wt.%: from 28.0 to 36.0% Zn; from 0.5 to 1.5% Si; from 1.5 to 2.5% Mn; from 0.2 to 1.0% Ni; from 0.5 to 1.5% Al; from 0.1 to 1.0% Fe; optionally up to 0.1% Pb, up to 0.1% P, and up to 0.08% S, with the balance being Cu and inevitable impurities, the copper-zinc alloy having incorporated therein mixed silicides of iron-nickel-manganese, a hard phase of the mixed silicides of iron-nickel-manganese being incorporated in an α-matrix and contributing to improving the resistance of the alloy against abrasive and adhesive wear; and after a post-processing step which involves hot-forming and further annealing steps, the alloy structure comprises both body-centered cubic crystal type β-phase inclusions in an amount of from 5-45 vol.% and the mixed silicides of iron-nickel-manganese present in an amount not exceeding 20 vol.% incorporated in the α-matrix, a portion of the mixed silicides of the iron-nickel-manganese having a columnar shape and a proportion of the iron-nickel-manganese mixed silicides having a globular configuration.

The invention includes the technical teaching that a copper-zinc alloy consists of (in wt%):

from 28.0 to 36.0% Zn,
from 0.5 to 2.3% Si,
from 1.5 to 2.5% Mn,
from 0.2 to 3.0% Ni,

from 0.5 to 1.5% Al,
from 0.1 to 1.0% Fe,
optionally also up to at most 0.1% Pb,
optionally also up to at most 0.2% Sn,
optionally also up to at most 0.1% P,
optionally also up to 0.08% S,
remainder Cu and inevitable impurities,

with mixed silicides of iron-nickel-manganese incorporated in the matrix.

The invention is based on the idea of providing a copper-zinc alloy which has incorporated mixed silicides of iron-nickel-manganese and can be produced with the aid of the continuous or semicontinuous extrusion casting method. Owing to the mixed silicide formation, the copper-zinc alloy has a high hard phase content which contributes to improving the material resistance against abrasive wear. Owing to their low susceptibility to seizure, the high content of silicides furthermore entails a better resistance against adhesive wear.

The alloy thus has high hardness and strength values but a requisite degree of ductility is nevertheless ensured, as expressed by an elongation at break value in a tensile test. With this combination of properties, the subject of the invention is particularly suitable for Pb-free friction bearing elements in engines, for example piston bore liners, and in transmissions.

When casting the alloy, early precipitation of iron- and nickel-rich mixed silicides initially takes place. During further growth, these precipitates can develop to form mixed silicides of iron-nickel-manganese with a considerable size, often with a columnar shape. Furthermore, a considerable proportion also remains rather small with a globular configuration, which is finely distributed in the matrix. In particular, the finely distributed silicides are regarded as the reason why stabilization of the β-phase takes place. This makes an important contribution to increasing the heat resistance and complex wear resistance.

The particular advantage of the alloy according to the invention is due to a combination of properties, optimized for an application purpose, in the form of increasing the strength, the heat resistance of the structure and the complex wear resistance while simultaneously having sufficient ductility properties. Furthermore, the alloy has good performance in the event of lubrication supply failure for friction bearing applications, which avoids seizure of the bearing partners. Owing to the substituted lead content compared with conventional alloys, the claimed material solution also accommodates the need for an environmentally friendly lead-free alloy alternative.

This material is furthermore intended for particular applications in which a requisite degree of plasticizability is important, despite stringent requirements for the hardness and strength. This is the case for example in the field of hydraulic equipment, the sliding pad of which is partly produced by pressing together the respective connection partners. Particularly in this field of hydraulic mechanical engineering, for example for axial piston machines, future developments are likely to entail increasing operating pressures which place greater demands on the strength properties of the materials being used.

In a preferred configuration, the alloy according to the invention may contain

from 28.0 to 36.0% Zn,
from 0.5 to 1.5% Si,
from 1.5 to 2.5% Mn,
from 0.2 to 1.0% Ni,
from 0.5 to 1.5% Al,
from 0.1 to 1.0% Fe.

Owing to the somewhat reduced elementary contents of silicon and nickel, the iron-nickel-manganese mixed silicide formation can be specially oriented toward an optimized combination of properties, particularly in relation to the requisite degree of ductility.

In another preferred configuration, the alloy according to the invention may contain

from 28.0 to 36.0% Zn,
from 1.0 to 2.3% Si,
from 1.5 to 2.5% Mn,
from 1.5 to 3.0% Ni,
from 0.5 to 1.5% Al,
from 0.1 to 1.0% Fe.

The ratio Mn/Ni of the elementary contents of the elements manganese and nickel may preferably lie between 0.7 and 1.3. With a higher silicon content, particularly in conjunction with the preferred Mn/Ni ratio, this material has good plasticizability. This is important particularly for friction bearing elements which need to receive their bearing partners by producing a press-fit connection just before operation.

Advantageously, the structure comprises a β-phase content of up to 50 vol.% in the cast state. This is regarded as a necessary prerequisite for sufficiently good hot formability of the copper alloy by extrusion.

In a preferred configuration of the invention, after post-processing which involves at least hot forming or cold forming and further annealing steps, the structure comprises a β-phase content of up to 45 vol.%, the mixed silicides of Fe-Ni-Mn up to 20 vol.% and a remainder of α-phase.

With these β-inclusions and hard phases of different size distribution in an α-matrix, this alloy ensures advantageous heat resistance of the structure with sufficient ductility properties as well as a suitable complex wear resistance of the components. In particular, owing to the low cold seizure susceptibility of silicides, the high silicide content contributes to improving the frictional and lubricant-failure properties in bearing elements, so that the omission of the Pb content can be compensated for. The demand for improved environmental compatibility of these machine and system components has therefore likewise been accommodated.

The ratio $R_{p0.2}/R_m$ of the values for the yield point and tensile strength of the alloy may advantageously lie between 0.5 and 0.95.

In the field of another application, i.e. hydraulic machine and system technology, future developments are likely to entail increasing stress on the friction bearings due to increasing operating pressures. Besides a strength increase, this configuration ensures the required ratio $R_{p0.2}/R_m$ in the range of between 0.5 and 0.95. This is an important prerequisite for the production of a bearing seat by press-fit connection of the friction bearing partners.

Another aspect of the invention relates to a method for producing tubes or rods made of the copper-zinc alloy according the invention, wherein a post-processing of the alloy comprises the following steps:

- extrusion in a temperature range of from 600 to 800°C,
- at least one cold forming.

These tubes and rods may be used as starting material for the machining manufacture of friction bearing elements.

Another alternative aspect of the invention relates to a method for producing tubes or rods made of the copper-zinc alloy according the invention, wherein a post-processing of the alloy comprises the following steps:

- extrusion in a temperature range of from 600 to 800°C,

- a combination of at least one cold forming with at least one anneal in a temperature range of from 250 to 700°C.

By means of a combination of cold forming by drawing and one or more intermediate anneals of the rods and tubes in the temperature range of from 250 to 700°C, it is possible to set up a fine distribution of the heterogeneous structure.

The demand for improving the complex operating properties of the bearing materials will thereby have been satisfied, since modern machines, engines, transmissions and equipment entail greatly increasing stress on the friction bearing elements. A significant increase in the tensile strength R_m, yield point $R_{p0.2}$ and hardness of the material are achieved with this particular configuration of the copper-zinc alloy. The elongation at break of the alloy likewise moves to a sufficiently high level, so that the required ductility properties are achieved. The extraordinarily high content of hard phases, in particular the mixed silicides of iron-nickel-manganese and the heterogeneous matrix structure of α- and β-phases, ensures a suitable complex wear resistance of the components made of this material.

The relationship between the level and distribution of the β-phase content and the heat resistance of the structure is already known. Yet since this body-centered cubic crystal type fulfills an indispensable strength-increasing function in the copper-zinc alloys, minimizing the β-content should not exclusively be paramount. By means of the manufacturing sequence of extrusion/drawings/intermediate anneals, the structure of the copper-zinc alloy can be modified in its phase distribution so that it also has a sufficient heat resistance besides a high strength.

In a preferred configuration, the forming may be followed by a stress-relieving anneal in a temperature range of from 250 to 450°C.

In the manufacturing procedure, it is necessary to reduce the level of residual stresses with the aid of one or more stress-relieving anneals. Reducing the residual stresses is also important for guaranteeing a sufficient heat resistance of the structure, and for ensuring sufficient straightness of the rods and tubes.

Furthermore, as already mentioned above, the copper-zinc alloy according to the invention may be used for friction bearing elements in combustion engines, transmissions or hydraulic equipment.

Further exemplary embodiments of the invention will be explained in more detail with the aid of the table. Cast bolts made of the copper-zinc alloy according to the invention were produced by ingot casting. The chemical composition of the castings is shown in Tab. 1.

Table 1: Chemical composition of the cast bolts (embodiment A)

No.	Cu [%]	Zn [%]	Si [%]	Mn [%]	Ni [%]	Sn [%]	Al [%]	Fe [%]
Alloy type 1	64.1	31.2	1.20	1.76	0.40	<0.01	0.92	0.30
Alloy type 2	63.6	31.7	1.17	1.75	0.55	<0.01	0.87	0.33
Alloy type 3	59.3	33.4	1.7	2.0	2.3	<0.01	0.9	0.5

Manufacturing sequence for alloy types 1 and 2:

- extrusion to form tubes at a temperature of 700°C
- combination of cold forming/intermediate anneals (650°C/50-60 min)/rectifying/stress-relieving anneals (300-350°C/3 h)

At the end of manufacturing, the mechanical properties of the tubes are at the level which is represented as numerical values in Tab. 2.

Table 2: Mechanical properties of the tubes (alloy type 1 and alloy type 2)

No.	β-content [%]	Grain size [µm]	R_m [MPa]	$R_{p0.2}$ [MPa]	$R_{p0.2}/R_m$	A5 [%]	HB
Alloy type	5	5-10	715	656	0.92	12.0	222

1							
Alloy type 2	5-10	10-15	660	577	0.87	13.2	207

Manufacturing sequence:

- Hot rolling at a temperature of 750°C on the laboratory scale
- Combination of cold forming/intermediate anneals (300-400°C/2-3 h)

At the end of manufacturing, the mechanical properties of the tubes are at the level which is represented as numerical values in Tab. 3.

Table 3: Mechanical properties (alloy type 3)

No. Alloy type 3	β-content [%]	Grain size [μm]	R_m [MPa]	$R_{p0.2}$ [MPa]	$R_{p0.2}/R_m$	A5 [%]	HB
Treatment 1 (300°C/2 h)	30-40	10	674	399	0.59	7.3	222
Treatment 2 (400°C/2 h)	30-40	10	621	424	0.68	13.1	206

What is claimed is:

1. A copper-zinc alloy, consisting of, in wt.%:

from 28.0 to 36.0% Zn;

from 0.5 to 1.5% Si;

from 1.5 to 2.5% Mn;

from 0.2 to 1.0% Ni;

from 0.5 to 1.5% Al;

from 0.1 to 1.0% Fe;

optionally up to 0.1% Pb, up to 0.1% P, and up to 0.08% S, with the balance being Cu and inevitable impurities, the copper-zinc alloy having incorporated therein mixed silicides of iron-nickel-manganese, a hard phase of the mixed silicides of iron-nickel-manganese being incorporated in an α-matrix and contributing to improving the resistance of the alloy against abrasive and adhesive wear; and

after a post-processing step which involves hot-forming and further annealing steps, the alloy structure comprises both body-centered cubic crystal type β-phase inclusions in an amount of from 5-45 vol.% and the mixed silicides of iron-nickel-manganese present in an amount not exceeding 20 vol.% incorporated in the α-matrix, a portion of the mixed silicides of the iron-nickel-manganese having a columnar shape and a proportion of the iron-nickel-manganese mixed silicides having a globular configuration.

2. The copper-zinc alloy according to claim 1, wherein the ratio $R_{p0.2}/R_m$ of the values for the yield point and tensile strength of the alloy lies between 0.5 and 0.95.

3. A method for producing tubes or rods made of a copper-zinc alloy defined in claim 1 or 2, wherein the post-processing of the alloy comprises the following steps:

   extrusion in a temperature range of from 600 to 800°C; and

   at least one cold forming.

4. The method for producing tubes or rods according to claim 3, wherein the post-processing of the alloy comprises a combination of at least one cold forming with at least one anneal in a temperature range of from 250 to 700°C.

5. The method according to claim 3 or 4, wherein the forming is followed by a stress-relieving anneal in a temperature range of from 250 to 450°C.

6. Use of a copper-zinc alloy defined in claim 1 or 2, for friction bearing elements in combustion engines, transmissions or hydraulic equipment.