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(54) **AGE-HARDENABLE COPPER ALLOY**

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(57) **ABSTRACT**

An age-hardenable copper alloy made of 1.2 to 2.7% cobalt, which is able to be partially replaced by nickel, 0.3 to 0.7% beryllium, 0.01 to 0.5% zirconium, optionally 0.005 to 0.1% magnesium and/or iron and in some instances up to a maximum of 0.15% of at least one element from the group including niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium. The remainder is copper and includes production-conditioned impurities and usual processing additives. This copper alloy is used as the material for producing mold blocks for the side dams of continuous strip-casting installations.

AGE-HARDENABLE COPPER ALLOY

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The invention relates to an age-hardenable copper alloy as material for producing blocks for the side dams of continuous strip-casting installations.

[0003] 2. Description of Related Art

[0004] The worldwide aim, especially in the steel and copper industries, to cast semifinished material to as close to the final dimensions as possible, in order to save hot forming and/or cold forming steps, led even before 1970 to the development of the so-called Hazelett strip-casting installations, in which the molten metal solidifies in the gap between two bands guided in parallel. The side dams in, for example, the strip-casting installation known from U.S. Pat. No. 3,865,176, are made of metallic mold blocks or dam blocks having a T groove, which are lined up on a flexible continuous band such as one made of steel, and which move in the longitudinal direction, synchronously with the casting bands. In this context, the dam blocks bound the casting mold cavity formed by the casting bands.

[0005] Also known, from EP 0 974 413 A1 are dam block chains for continuous strip-casting, formed by blocks having a slot and key. The advantage of these further developed mold blocks having a slot and key comes about due to a more exact alignment and guidance of the blocks during the casting process, and leads to an improvement of the surface quality of the cast strip. In order to prevent premature wear of the side edges of the blocks by plastic deformation and the formation of cracks, a suitable material has to have great hardness and strength, a fine-grained microstructure and a good long-term resistance to softening. In order to remove the heat of solidification from the liquid molten material, a high thermal conductivity of the mold block material is additionally required.

[0006] Finally, optimum fatigue behavior of the material is of the most decisive significance, which will ensure that, after leaving the casting segment, the thermal stresses appearing during the cooling off of the blocks do not lead to cracking of the blocks at the corners of the T groove incorporated for the accommodation of the steel band. In this context, particularly great thermal stresses are to be expected in dam blocks having the design using slot and key, on account of the unfavorable geometry and mass distribution.

[0007] If such cracks caused by thermal shock appear, the respective mold block will fall out of the dam block chain of the continuous strip-casting machine after even a short period, molten metal being able to run uncontrollably from the casting mold cavity and to damage parts of the installation. For the purpose of exchanging the damaged mold blocks, the entire strip-casting installation has to be stopped and the casting process has to be interrupted.

[0008] A testing method has proven itself for checking the tendency to crack, in which the mold blocks are submitted to heat treatment for two hours at 500° C. and are subsequently quenched in water at 20 to 25° C. Even if this thermal shock test is repeated several times, in the case of a suitable material no cracks may appear in the T groove surface.

[0009] EP 0 346 645 B1 describes an age-hardenable copper-based alloy which is made of 1.6 to 2.4% nickel, 0.5 to 0.8% silicon, 0.01 to 0.2% zirconium, optionally up to 0.4% chromium and/or up to 0.2% iron, the remainder being copper including production-caused impurities. This known copper alloy basically satisfies the prerequisites for a long service life, if used as the material for producing standard mold blocks for the side dams of continuous strip-casting installations. The following combination of properties is given for this copper alloy:

Rm at 20° C.:	635 to 660 MPa
Rm at 500° C.:	286 to 372 MPa
Brinell hardness:	185 to 191 HB (corresponds to about 195 to 210 HV)
Conductivity:	41.4 to 42.4% IACS.

[0010] No cracks are to appear during the thermal shock test. One advantage compared to beryllium-containing copper-based alloys is the possibility of being able to regrind the mold blocks manually, since no beryllium is contained in the grinding dust. The reprocessing of used dam blocks having slot and key is considerably more costly and, as a rule, requires machine (wet) cleaning of the T groove and the casting surfaces (e.g. in closed chambers), whereby the liberation of grinding dusts is prevented. Thus, using beryllium-containing alloys would basically be possible under these circumstances.

[0011] A dam block made of the CuNiSiZr alloy described in EP 0 346 645 81, however, disadvantageously tends to premature wear of the side edges and casting surfaces, at very high mechanical and thermal stresses in the casting operation of a continuous strip-casting installation. As the results of investigations have shown, this wear may be attributed to a material softening of the casting edges and surfaces to a value below 160 HV. Furthermore, the thermal shock resistance of the known CuNiSiZr alloy is not always sufficient for effectively preventing the formation of cracks in the T groove during casting use, when the alloy is used for a dam block having a slot and key.

SUMMARY OF THE INVENTION

[0012] It is an object of the invention to create an age-hardenable copper alloy as a material for producing dam blocks for continuous strip-casting installations, especially in a slot and key embodiment, which is stable to changing temperature stresses even at high casting speeds, and which has a great resistance to wear and resistance to softening, as well as great resistance to crack formation in the T groove.

[0013] These and other objects of the invention are achieved by an age-hardenable copper alloy made of 1.2 to 2.7% cobalt, 0.3 to 0.7% beryllium, 0.01 to 0.5% zirconium, optionally 0.005 to 0.2% magnesium and/or 0.005 to 0.2% iron and, in some instances, up to a maximum of 0.15% of at least one element from the group including niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium, the remainder being copper including production-caused impurities and the usual processing additives. This alloy is used as the material for producing block for the side dams of strip-casting installations.

DETAILED DESCRIPTION OF THE INVENTION

[0014] By using a copper-based alloy made of 1.2 to 2.7 wt. % cobalt, 0.3 to 0.7 wt. % beryllium, 0.01 to 0.5 wt. % zirconium, optionally 0.005 to 0.2 wt. % magnesium and/or iron and of the remainder copper, including production-caused impurities and the usual processing additives, on the one hand, a sufficient age-hardenability of the material for achieving great strength, hardness and conductivity may be ensured. On the other hand, only a relatively slight cold working of up to a maximum of 40% is required for establishing a fine-grained microstructure having a sufficient plasticity. Because of the deliberately graduated zirconium content, both the fatigue resistance and the heat resistance properties are improved.

[0015] A further improvement of the mechanical properties of the dam blocks, especially an increase in tensile strength, may advantageously be achieved by having the copper alloy contain 1.8 to 2.4 wt. % cobalt, 0.45 to 0.65 wt. % beryllium, 0.15 to 0.3 wt. % zirconium, up to 0.05 wt. % magnesium and/or up to 0.1% iron.

[0016] The invention permits that, in the copper alloy up to 80% of the cobalt content may be replaced by nickel.

[0017] Further improvements of the mechanical properties of a dam block may be achieved if the copper alloy contains up to a maximum of 0.15 wt. % of at least one elements of the group including niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium. Usual deoxidants such as boron, lithium, potassium and phosphorus may also be added up to a maximum of 0.03 wt. %, without negatively influencing the mechanical properties of the copper alloy of the present invention.

[0018] According to another specific embodiment, a part of the zirconium content may be replaced by up to 0.15 wt. % by at least one element of the group including cerium, hafnium, niobium, tantalum, vanadium, chromium, manganese and titanium.

[0019] Advantageously, the blocks for the side dams of double strip-casting installations are produced using the age-hardenable copper alloy, by the method steps: casting, hot forming, cold forming up to 40%, solution treating at a temperature in the range of 850 to 970° C., as well as a 0.5 to 16-hour age-hardening treatment at 400 to 550° C.

[0020] As a particular advantage, the copper alloy may be cold formed by 5 to 30% after hot forming. A cold forming degree of 10 to 15% lying within this range is particularly preferred in this context.

[0021] It is especially advantageous if the dam blocks in the age-hardened condition have a tensile strength of at least 650 Mpa, particularly 700 to 900 Mpa, a Vickers hardness of at least 210 HV, particularly 230 to 280 HV, an electrical conductivity of at least 40% IACS, particularly 45 to 50% IACS, a hot tensile strength at 500° C. of at least 400 Mpa, particularly of at least 450 Mpa, a minimum hardness of 160 HV after 500-hour ageing at 500° C., and a maximum grain size according to ASTM E 112 of 0.5 mm.

[0022] Particularly preferred are dam blocks made of the copper alloy, if, in the age-hardened condition they have a grain size, ascertained according to ASTM E 112, between 30 and 90 μm.

[0023] In a preferred embodiment, the copper alloy, after the hot forming of the cast blank, is cold formed up to 40%, is then solution treated at a temperature lying in the temperature range of 850 to 970° C., and is subsequently submitted to a 0.5 to 16-hour age-hardening treatment at 400 to 550° C. In a surprisingly simple way one may succeed in getting rid of the bad recrystallization behavior observed in the known CuCoBe alloys during the hot forming and solution treatment. The bad recrystallization behavior, in the production of mold blocks made of CuCoBe alloys, in the hot formed, solution treated and age-hardened condition leads to a coarse microstructure, that is not acceptable for the application purpose, having grain sizes up to more than 1 mm. However, if, between the hot forming and the solution treatment, the material is submitted to cold forming up to a maximum of 40%, preferably up to a maximum of 15%, this additional processing step leads to a considerably more fine-grained microstructure. Relevant investigative series have confirmed that materials for mold blocks for the side dams of strip-casting machines, which are cold formed below the recrystallization temperature, and are subsequently solution treated, have a clearly finer microstructure at grain sizes below 0.5 mm, while higher degrees of cold forming, above approximately 40%, lead during subsequent solution treatment to a coarsening of the grain by secondary recrystallization, at grain sizes above 1 mm.

EXAMPLES

[0024] The invention is explained below in greater detail, with the aid of exemplary embodiments. The advantages of the copper alloys are demonstrated using three alloys according to the invention (A, B and C) and three alloys for reference (D, E and F). The composition of the copper alloys in wt. % is given below in Table 1.

TABLE 1

Alloy	Co (%)	Ni (%)	Be (%)	Zr (%)	Si (%)	Cr (%)	Cu (%)
A	2.1	—	0.54	0.18	—	—	Remainder
B	2.2	—	0.56	0.24	—	—	Remainder
C	1.3	1.0	0.48	0.15	—	—	Remainder
D	—	2.0	—	0.16	0.62	0.34	Remainder
E	2.1	—	0.55	—	—	—	Remainder
F	1.0	1.1	0.62	—	—	—	Remainder

[0025] In the case of the composition of alloy D, a known CuNiSi-based alloy is involved, whereas E and F are normalized CuCo2Be or CuCoNiBe materials.

[0026] All the copper alloys were smelted in an induction crucible oven and were cast by the continuous strip-casting method to round billets having a diameter of 280 mm. The round billets of exemplary alloy A, B and C were extruded on an extrusion press at a temperature above 900° C. to flat bar of a dimension 79×59 mm, and subsequently were drawn, at a loss in cross section of 12%, to a dimension of 75×55 mm. The blocks of the reference alloys D, E and F were extruded at the same temperature, directly to the dimension 75×55 mm, and were not submitted to additional cold forming. The CuCoBe and CuCoNiBe materials were subsequently solution-treated at 900 to 950° C. and were age-hardened at a temperature range between 450 and 550° C. for 0.5 to 16 hours.

[0027] The CuNiSi-based alloy was solution-treated at 800 to 850° C. and age-hardened under the same conditions. In the age-hardened condition, the tensile strength Rm, the Vickers hardness HV10, the electrical conductivity (as substitute quantity for the heat conductivity), the grain size according to ASTM E112, the heat resistance Rm at 500° C. and the resistance to softening via Vickers hardness measurement (HV10) after ageing at 500° C. after 500 hours were ascertained.

[0028] The thermal shock behavior was finally tested on mold blocks (1) of dimensions 70×50×40 mm and mold blocks (2), having slot and key, of dimensions 70×50×47 mm. For this, the mold blocks were first annealed for two hours at 500° C. and then quenched in water at 20 to 25° C. The T groove of the blocks were then searched for cracks with the naked eye and a microscope at 10-fold magnification.

[0029] All the test results are summarized in Table 2 below.

TABLE 2

Alloy	Tensile Strength MPa	Vickers Hardness HV10	Conductivity (electrical) % IACS	Grain Size μm	Strength (500° C.) MPa	Vickers Hardness 10 After Ageing at 500° C. over 500 h	Behavior After Thermoshock Test Block (1)	Block (2)
A	801	254	50	30–90	523	173	crack-free	crack-free
B	804	245	51.5	45–90	464	175	crack-free	crack-free
C	812	255	49.5	45–90	485	167	crack-free	crack-free
D	652	205	43	45–90	387	118	crack-free	cracked
E	786	260	50.5	to 5000	423	150	cracked	cracked
F	807	248	48.5	to 3000	434	152	cracked	cracked

[0030] In the mold blocks classified as "cracked", the extension of determined cracks in the groove was 2 to 5 mm, and in individual cases, the length of the crack was up to 10 mm. One may see from the reference that, as compared to materials E and F, only copper alloys A, B and C, and produced using slight cold working, at optimum properties, have a surprisingly uniform and fine-grained microstructure, and have the necessary resistance to the formation of cracks when used as mold block having slot and key. Even when used in a usual mold block, the copper alloys in accordance with the invention have a clearly better resistance to softening compared to the known CuNiSi alloys D, and a somewhat better resistance to softening when compared to alloys E and F.

[0031] Therefore, the copper alloy in accordance with the invention is eminently suitable as the material for producing all mold blocks, that are submitted to typically changing temperature stress during the casting process, for the side dams of strip-casting installations. These are both the mold blocks used up to the present and the mold blocks embodied with slot and key as in EP 0 974 413 A1.

What is claimed is:

1. An age-hardenable copper alloy suitable as a material for producing block for the side dams of strip-casting installations, comprising: 1.2 to 2.7% cobalt, 0.3 to 0.7% beryllium, 0.01 to 0.5% zirconium, and a balance of copper.

2. The copper alloy according to claim 1, further comprising 0.005 to 0.2% magnesium.

3. The copper alloy according to claim 1, further comprising 0.005 to 0.2% iron.

4. The copper alloy according to claim 2, further comprising 0.005 to 0.2% iron.

5. The copper alloy according to claim 1, further comprising up to a maximum of 0.15% of at least one element selected from the group consisting of niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium.

6. The copper alloy according to claim 2, further comprising up to a maximum of 0.15% of at least one element selected from the group consisting of niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium.

7. The copper alloy according to claim 3, further comprising up to a maximum of 0.15% of at least one element selected from the group consisting of niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium.

8. The copper alloy according to claim 4, further comprising up to a maximum of 0.15% of at least one element selected from the group consisting of niobium, tantalum, vanadium, hafnium, chromium, manganese, titanium and cerium.

9. The copper alloy according to claim 4, comprising: 1.8 to 2.4% cobalt, 0.45 to 0.65% beryllium, 0.15 to 0.3% zirconium, up to 0.05% magnesium, up to 0.1% iron, and a balance of copper.

10. The copper alloy according to claim 1, wherein up to 80% of the cobalt content is replaced by nickel.

11. The copper alloy according to claim 2, wherein up to 80% of the cobalt content is replaced by nickel.

12. The copper alloy according to claim 1, wherein a part of the zirconium content is replaced by up to 0.15 wt. % of at least one element selected from the group consisting of cerium, hafnium, niobium, tantalum, chromium, manganese, titanium and vanadium.

13. The copper alloy according to claim 2, wherein a part of the zirconium content is replaced by up to 0.15 wt. % of at least one element selected from the group consisting of cerium, hafnium, niobium, tantalum, chromium, manganese, titanium and vanadium.

14. The copper alloy according to claim 1, which, after hot forming of the cast blank, is cold formed up to 40%, is then solution treated at a temperature lying in the temperature range of 850 to 970° C., and is subsequently submitted to a 0.5 to 16-hour age-hardening treatment at 400 to 550° C.

15. The copper alloy according to claim 14, which, after the hot forming, is cold formed by 5 to 30%.

16. The copper alloy according to claim 14, which, after hot forming, is cold formed by 10 to 15%.

17. The copper alloy according to claim 1, which, in the age-hardened state, has a tensile strength of at least 650 Mpa, a Vickers hardness of at least 210 HV, an electrical conductivity of at least 40% IACS, a hot tensile strength at 500° C. of at least 400 Mpa, a minimum hardness of 160 HV after 500 hours of constant ageing at 500° C. and a maximum grain size according to ASTM E112 of 0.5 mm.

18. The copper alloy according to claim 1, which, in the age-hardened state, has a tensile strength of at least 700 to 900 Mpa, a Vickers hardness of 230 to 280 HV, an electrical conductivity of 45 to 60% IACS, a hot tensile strength at 500° C. of at least 450 Mpa and a minimum hardness of 160 HV after 500 hours of constant ageing at 500° C.

19. The copper alloy according to claim 1, which has a grain size between 30 and 90 μm, ascertained according to ASTM E112.

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