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(54) **CONTINUOUS CASTING MOLD AND METHOD OF CONTINUOUS CASTING FOR COPPER ALLOY**

(57) A continuous casting mold for a Cu alloy, using any one member selected from a glassy carbon, a metal-based self-lubricating composite or a graphite with a bulk density exceeding 1.92, at least for the mold member including the solidification starting position of the Cu alloy melt.

A continuous casting mold for a Cu alloy, composed of any one member selected from a graphite, a ceramic and a metal member or of a combination of two or more parts of members thereof, in which at least the inner wall in the solidification starting position of the Cu alloy melt

is coated with a self-lubricant or a metal-based self-lubricating composite material.

A continuous casting method of a Cu alloy, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the slab intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction of the slab, or continuously supplying a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

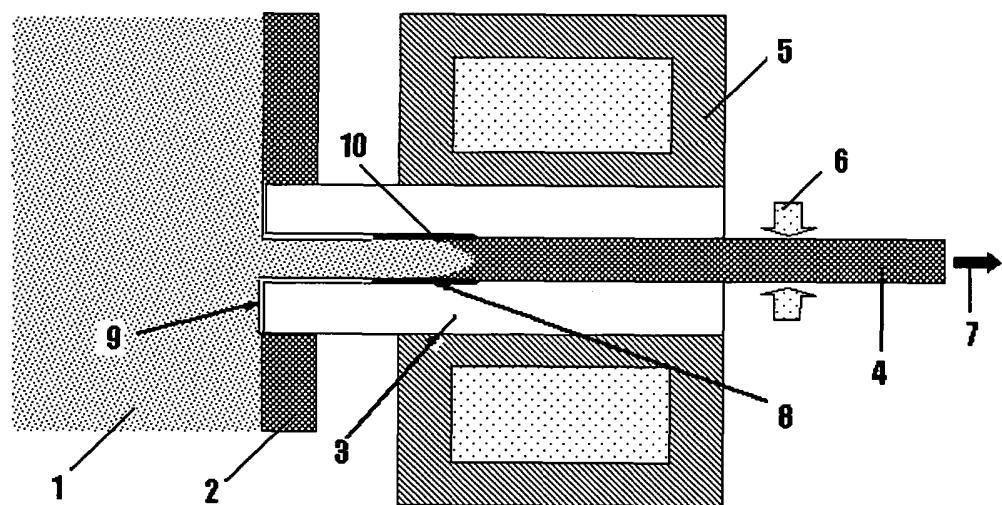


Fig.7

Description

[Technical Field]

5 [0001] The present invention relates to a continuous casting mold and a continuous casting method of a Cu alloy, particularly, a casting mold used for a direct-connection type of continuous casting machine, in which a mold is directly connected to a holding furnace, and a continuous casting method of a Cu alloy using this mold.

[Background Art]

10 [0002] Along with the recent development of Information Technology, particularly, in the technology of the cellular phone, portable computer or the automobile electronic equipment, it has become more important to enhance the performance of a Cu alloy used for electric and electronic parts such as a lead frame, a terminal, a connector, a spring or a contact element. The typical first necessary characteristic is higher strength for a reduction in weight, and the second is higher electric conductivity for suppressing a rise of electric resistance caused by reduction in the sectional area due to the reduction in weight. On the other hand, the improvement in workability such as bending workability due to the downsizing of parts, the improvement in heat resistance in order to ensure usability even in relatively severe environments, and the improvement in fatigue strength are also important problems.

15 [0003] Such a highly strong and highly electric-conductive material can also be applied to safety tool materials used in an environment such as an ammunition chamber or a coal mine which needs excellent spark generation resistance, in addition to the wear resistance needed for conventional tools. Such a material is exemplified the Cu alloy disclosed in the Patent Document 1 below.

20 [0004] Continuous casting of a Cu alloy executed mainly in two methods is described below.

25 [0005] The first method is a direct-connection type of continuous casting including horizontal type and vertical type casting, using a graphite-made mold directly connected to a holding furnace. Since a supply of a lubricant is extremely difficult in the direct-connection type of continuous casting, graphite with a bulk density of 1.7 to 1.9, which has a self-lubricating property and high heat conductivity, has widely been used for the mold material. This method is suitable for obtaining a slab or a bloom with relatively small sectional area. In such type of continuous casting process, the cooling rate after solidification is relatively high, leading to a high performance of a final product even without a subsequent hot process such as a solution treatment or a hot working.

30 [0006] The second method is a non-direct-connection type of continuous casting including vertical type, curved type and vertical-curved type casting, described in the Patent Document 1, in which melt is poured into a mold made of a metal such as Cu or an alloy such as a Cu alloy through a nozzle immersed into a melt pool. In the non-direct-connection type of continuous casting, the slabs to be cast are limited to a relatively large size with a thickness of about 100 mm or more, since the nozzle can be immersed into the melt pool within the mold. This method essentially requires a hot process such as a solution treatment or a hot working in the later production process because of a low cooling rate in the cooling process after solidification.

35 [0007] A proper method is selected from these two kinds of continuous casting methods according to the required alloy composition, slab sectional shape, cooling rate, or the like. In general, the former direct connection type is adapted when a high cooling rate is needed or when the Cu alloy is free from highly reactive elements with C in the graphite. The latter non-direct connection type is adapted when a slab of a large sectional size is needed or when the Cu alloy contains highly reactive elements with C in the graphite.

40 [0008] [Patent Document] Japanese Patent Unexamined Publication No. S61-250134.

45 [Disclosure of the Invention]

[Problem to be Solved by the Invention]

50 [0009] The primary objective of the present invention is to provide a continuous casting mold suitable for a direct-connection type of continuous casting of the Cu alloy containing elements such as Zr, Ti, and Cr that are reactive with C. The second objective of the present invention is to provide a continuous casting method of the Cu alloy using the above-described mold. The continuous casting mold of the present invention is highly effective for continuous casting not only of Cu alloys but also of such materials as non-ferrous metals other than Cu alloys.

55 [Means for Solving the Problems]

[0010] In many cases, new Cu alloys intended for higher strength and higher electric conductivity contain elements such as Zr, Ti and Cr, which easily react with C. They also need a high cooling rate in the cooling process after solidification

in order to attain satisfactory characteristics of the final products. However, these alloys are found to have the following problems, which results from the reaction of above-mentioned elements with C in the graphite mold.

[0011] In the application of the above-mentioned Cu alloys to the direct-connection type of continuous casting, the elements such as Zr, Ti and/or Cr in the melt, which are reactive with C in the graphite, results in a sticking of the initially formed solidification shell to the mold, with remarkable increase of the pulling out resistance. As a result, problems such as a mold damage due to the sticking and a surface cracking of the slab are often caused. The application of these kinds of alloys to the direct-connection type of continuous casting is thus quite difficult. This is also the reason why the development of the high performance alloy using the conventional process has been restricted.

[0012] To solve these problems, the present invention relates to a continuous casting mold, capable of providing a sufficiently high cooling rate in the cooling process after solidification, while suppressing the sticking of the initially formed solidification shell to the mold, and a continuous casting method using the mold, and involves the following inventions of continuous casting molds (1) to (5) and inventions of continuous casting methods (6) to (14). These inventions are hereinafter referred to as the present inventions (1) to (14), respectively, or often are referred to collectively as the present invention.

[0013] (1) A continuous casting mold for a Cu alloy, using any one member selected from a glassy carbon, a metal-based self-lubricating composite or a graphite with a bulk density exceeding 1.92, at least for the mold member including the solidification starting position of the Cu alloy melt.

[0014] (2) A continuous casting mold for a Cu alloy, composed of any one member selected from a graphite, a ceramic and a metal member or of a combination of two or more parts of members thereof, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material.

[0015] (3) A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which the self lubricant or the metal-based self-lubricating composite member is used at least for the inner wall in the solidification starting position of the Cu alloy melt.

[0016] (4) A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material.

[0017] (5) The continuous casting mold for a Cu alloy according to any one of (1) to (4) above, wherein the inner wall in the position that contacts with the Cu alloy melt is coated with a ceramic material.

[0018]

(6) A continuous casting method of a Cu alloy, comprised of performing continuous casting by an intermittent pulling out method, by use of any one of the molds described in (1) to (5) above.

(7) A continuous casting method of a Cu alloy, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the slab intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction of the slab.

(8) A continuous casting method of a Cu alloy, comprised of continuously supplying, at the time of the continuously casting the Cu alloy by an intermittent pulling out method, a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

(9) A continuous casting method of a Cu alloy, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the slab intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction to a mold, and continuously supplying a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

[0019] (10) A continuous casting method of a Cu alloy according to (6) above, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction of the slab.

[0020] (11) A continuous casting method of a Cu alloy according to (6) or (10) above, comprised of continuously supplying, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

[0021] (12) A continuous casting method of a Cu alloy according to any one of (6) to (11) above, wherein the Cu alloy contains, by mass %, one or more components selected from Cr: 0.01 to 5%, Ti: 0.01 to 5%, Zr: 0.01 to 5%, Nb: 0.01 to 5%, Ta: 0.01 to 5%, Al: 0.01 to 5%, Mo: 0.01 to 5%, V: 0.01 to 5%, Co: 0.01 to 5%, Mn: 0.01 to 5%, Si: 0.01 to 5%, Be: 0.01 to 5%, and Hf: 0.01 to 5%.

[0022] (13) A continuous casting method of a Cu alloy according to (12) above, wherein the Cu alloy further contains,

by mass%, 0.001 to 5 % in total of one or more of alloy components selected from at least one group of the following three groups:

5 First group: 0.001 to 1 mass% in total of one or more selected from P, B, Sb, Bi, Pb, Cd, S and As;

Second group: 0.01 to 5 mass% in total of one or more selected from Sn, Ag, Zn, Ni, Au, Pd, Fe, W, In and Ge; and

Third group: 0.01 to 3 mass% in total of one or more selected from Te, Se, Sr, T1, Rb, Cs, Ba, Re, Os, Rh, Po, Ga, Tc, Ru, Pd, Ir, Pt and Ta.

10 [0023] (14) A continuous casting method of a Cu alloy according to (12) or (13) above, wherein the Cu alloy further contains, by mass %, 0.001 to 2% in total of one or more of alloy components selected from Li, Ca, Mg and rare earth elements.

[Effect of the Invention]

15 [0024] According to the present invention, a continuous casting mold capable of continuously and stably producing a sound slab can be provided. A continuous casting method of a Cu alloy capable of ensuring excellent characteristics such as strength, electric conductivity, bending workability and fatigue strength of the final product after working and heat treatment, can be provided. Particularly, in application to casting of a Cu alloy containing Zr, Ti, Cr, Ta, V and so on, which are elements that easily form into carbides, a profound effect can be obtained. The present invention is highly effective not only for Cu alloys but also for such materials as non-ferrous metals other than Cu alloys.

[Best Mode for Carrying out the Invention]

20 [0025] Preferred embodiments of the present invention will be described.

25 <Mold of the Present Invention>

30 [0026] Examples of a mold for a direct-connection type of horizontal continuous casting according to the present invention, are shown in Figs. 1 to 7. In each figure, the mold is directly connected to a refractory constructing the holding furnace wall 2 that stores a Cu alloy melt 1. In order to protect the connection part of the holding furnace wall, a connecting refractory, such as a feeding nozzle, may be provided between the holding furnace wall and the mold. A cooling jacket 5, adapted to carry cooling water or the like into the mold, is arranged closely to the outside of a mold member 3 and/or another part of mold member 3', in which heat extraction is performed by primarily cooling the Cu alloy melt, and the solidification proceeds to form into a slab 4. The slab 4 leaving the mold is subjected to secondary cooling 6 by water spray, air spray, air-water mixed spray or the like. The slab 4 is pulled out in an arrowed direction 7.

35 [0027] The mold according to the present invention may include a coating 8 applied to the inner wall of the mold in the solidification starting position 10 of the Cu alloy melt. It may include a coating 9 applied to the inner wall in the position of the mold, which is located at an upper stream part than the solidification starting position.

40 The mold may be composed of a plurality of parts of mold members, for example, a part of mold member 3 and another part of mold member 3'.

45 [0028] The mold inner wall might be deteriorated by oxidation at the time of preheating before casting. In order to prevent this deterioration, an oxidation resisting coating such as metal plating, is preferably applied at least to the inner wall of the mold in the solidification starting position of the inner wall surface of the mold. The oxidation resisting coating material is not particularly limited, but one easily soluble to the melt at the time of casting without deteriorating the characteristics or the like of the final product, is preferably used. In casting of the Cu alloy, for example, Cu is preferably used as the coating material, with a thickness of about several micrometers.

50 [0029] The solidification starting position in the present invention is defined as follows. In the mold, molten Cu alloy is fed from the holding furnace, and forms into a solidification shell in a certain position in the mold. This solidification shell forming position is called the solidification starting position. The solidification starting position is slightly varied depending on the casting conditions such as the temperature of the melt in the holding furnace, the cooling condition in both primary and secondary stages, and the pulling out velocity and so on. Thus, the solidification starting position has a certain fluctuation in the pulling out direction.

55 [0030] Figures 1 to 7 show examples of the mold for a direct-connection type of horizontal continuous casting according to the present invention, while the mold for a direct connection type of vertical continuous casting can be shown by rotating these figures clockwise by 90°.

[0031] A continuous casting mold for a Cu alloy according to the present invention will be further described in detail in terms of types (A) to (E). Further, a method for continuously casting a Cu alloy by use of these molds will also be described.

[0032] (A) A continuous casting mold for a Cu alloy, using any one member selected from a glassy carbon, a metal-based self-lubricating composite or a graphite, at least for the mold member including the solidification starting position of the Cu alloy melt:

[0033] Figure 1 is a schematic view of a continuous casting mold for a Cu alloy as one example of the continuous casting mold, according to the present invention, using a glassy carbon, a metal-based self-lubricating composite or a graphite material for the mold member 3 including the solidification starting position 10 of the Cu alloy melt.

[0034] By using the glassy carbon, the metal-based self-lubricating composite or the graphite material, at least for the mold member including the solidification starting position of the Cu alloy melt, a sound slab can be produced continuously, efficiently, and stably. The graphite member preferably has a bulk density exceeding 1.92.

10 A continuous casting method of a Cu alloy capable of ensuring excellent characteristics such as strength, electric conductivity and fatigue strength of a final product after working and heat treatment, can be provided. Particularly, in application to casting of the Cu alloy containing elements such as Zr, Ti, Cr, Ta and V, which easily form into carbides, a profound effect can be obtained.

15 [0035] The present inventors found that, when the direct-connection type of continuous casting is executed using a mold member which is made of a conventional graphite material with a bulk density of 1.7 to 1.9, the Cu alloy melt penetrates into a number of open pores which are on the graphite surface, whereby the initially formed solidification shell is stuck to the mold, resulting in mold damage with increase of the pulling out resistance or sometimes into an interruption of process. It was also found that, when the melt contains elements such as Zr, Ti and Cr which are reactive with C, the formation of the carbides in the boundary between the melt and the mold further causes sticking of the initially formed solidification shell to the mold, resulting in mold damage due to mold biting or into an interruption of the slab pulling out process.

20 [0036] It is found effective for solving these problems to use either of the mold material (a) that rarely reacts with the elements in the melt and the mold material (b) that has very few small sizes of open pores on the surface..

25 [0037] Namely, at first, use of a glassy carbon or a metal-based self-lubricating composite material is effective from the viewpoint of the reaction between the mold material and the melt.

The glassy carbon material has characteristics of being, rarely oxidized, compared with the graphite, and also being rarely reactive with Zr, Ti, and Cr, and therefore, it was found that the purpose can be sufficiently attained.

30 [0038] The metal-based self-lubricating composite material means a cermet obtained by dispersing and mixing a self-lubricant such as M_2S_2 , WS_2 , BN or mica that rarely reacts with Ti, Cr or Zr into a metal matrix. This composite material can also sufficiently attain the purpose.

The method for producing the composite material is not particularly limited. For example, mixing a metal powder with a self-lubricant particle, followed by pressing and sintering, can produce the composite material.

35 The content of the self-lubricant in the composite material is not particularly limited, but is, by volume %, preferably 10% or more, more preferably 30% or more, and further preferably 80% or more. Although an increased content of the self-lubricant leads to an improvement in the reaction resistance and the lubricating property, it causes the deterioration of the mechanical properties such as strength and heat impact resistance, therefore the content is, by volume %, preferably controlled to 85 % or less.

40 The metal constituting the composite material with the self-lubricant is not particularly limited, and any metal or alloy can be used. Use of a metal and/or an alloy having a high melting point and high thermal conductivity is preferred since the mold material makes contact with a Cu alloy melt. The specific examples of the metal of the alloy are a Cu alloy, a stainless steel, a Ni alloy, a Co alloy, and a W alloy.

[0039] Secondly, it is effective to use a high-bulk density graphite with very few open pores. As a result of various studies, it was found that the purpose can be sufficiently attained with a bulk density exceeding 1.92.

45 [0040] In continuous casting of a Cu alloy by means of an intermittent pulling out method by use of this mold, a further profound effect can be obtained by adopting either or both of measures of (1) giving a vibration that has a frequency larger than the intermittent frequency by two orders or more and that has a component vertical to the pulling out direction of the slab and (2) continuously supplying a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

50 Since the sticking of the slab surface to the mold can be prevented by adopting either or both of the measures (1) and (2), even if a graphite with a bulk density of less than 1.92 is used as the material used in the mold, continuous casting can be performed.

The preventing effect of the sticking is further improved by using a graphite with a bulk density exceeding 1.92 as the material constituting the mold in addition to either or both of the measures (1) and (2).

55 [0041] According to the intermittent pulling out method, since the frictional resistance between the mold inner wall and the slab is reduced in terms of the lubricating effect, a sufficiently sound slab can be continuously, efficiently, and stably produced.

[0042] If a vibration that has a frequency larger than the intermittent frequency by two orders or more and that has a component vertical to the pulling out direction is given to the mold, the similar effect can be obtained over a longer time.

An increased vibration frequency is more preferable, and it is preferably set to 5000 cpm (83 Hz) or more, and more preferably to 60000 cpm (1 kHz) or more, which is close to the ultrasonic area.

[0043] It is recommended to use a fine particle of MoS_2 , WS_2 , BN, mica, or carbon as the lubricant to be supplied between the mold inner wall and the slab. Among them, a superfine particle of CaCO_3 , which is difficult to agglomerate, is strongly recommended as the anti-sticking material. The continuous supply thereof is performed, for example, by injecting a solution of the fine particle of the lubricant or anti-sticking material suspended in mineral oil, synthetic ester or a mixture thereof through a number of through-holes of about 20 μm provided in the mold inner wall by the use of a pressure pump. A sufficient effect can be obtained in an injection quantity of about 0.1 cc/cm²·min, which is as little as sweat.

[0044] (B) A continuous casting mold for a Cu alloy, composed of any one member selected from a graphite, a ceramic and a metal member or of a combination of two or more parts of members thereof, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material:

[0045] Figure 2 is a schematic view of a continuous casting mold for a Cu alloy as an example of the continuous casting mold according to the present invention, in which the mold member 3 is composed of any one member selected from a graphite, a ceramic and a metal, and in which a coating 8 of a self-lubricant or a metal-based self-lubricating composite material is applied to the inner wall in the solidification starting position 10 of the Cu alloy melt.

[0046] A mold which is composed of any one member selected from the graphite, the ceramic and the metal member, with a coating of the self-lubricant or the metal-based self-lubricating composite material applied to the inner wall of the mold, is used, whereby a sound slab can be continuously, efficiently and stably produced.

A continuous casting method of a Cu alloy capable of ensuring excellent characteristics such as strength, electric conductivity and fatigue strength of the final product after working and heat treatment, can be provided. Particularly, in application to casting of a Cu alloy containing elements such as Zr, Ti, Cr, Ta and V, which easily form into carbides, a profound effect can be obtained.

[0047] When the graphite is selected as the mold material, a compact coating material composed of C, for example, a glassy carbon, a layered carbon and a diamond-like carbon, which are self-lubricant materials, are preferably selected in order to enhance the adhesion between the mold material and the coating film. Since the surface unevenness of the coating film almost reflects the surface unevenness of the graphite itself, it is desirable to select a graphite with a bulk density as high as possible. Although the bulk density is not particularly limited, it is preferably 1.7 or more, more preferably 1.8 or more, or further preferably more than 1.92.

[0048] As the ceramic, an inorganic material composed of one or more selected from oxides, nitrides, carbides and borides is used. Although it is not particularly limited, a BN material and a sialon material (a compound consisting of Si, Al, O, and N, shown by a phase diagram of $\text{Si}_3\text{N}_4\text{-AlN}\text{-Al}_2\text{O}_3\text{-SiO}_2$) are preferable because of the mechanical strength and thermal conductivity to be provided as the mold material.

[0049] When a material with low thermal conductivity is used, the thinner mold thickness, that is, the narrower distance between the slab and a cooling jacket is preferably adapted. When a ceramic composed of sintering BN and sialon is selected, a compact coating material composed of a nitride compound, for example, a BN material that is a self-lubricant is preferably selected in order to enhance the adhesion between the mold material and the coating film.

[0050] The metal is not particularly limited, and any metal or alloy can be used. Use of a metal or an alloy having a high melting point and high thermal conductivity is preferred, for example, a Cu alloy, a stainless steel, a Ni alloy, a Co alloy, a W alloy, since the mold material will make contact with the Cu alloy melt. When the metal is selected, a metal-based compact coating material such as a metal-based self-lubricant material is preferably selected in order to enhance the adhesion between the mold material and the coating film.

[0051] The metal-based self-lubricating composite material means a cermet obtained by dispersing and mixing a self-lubricant such as MoS_2 , WS_2 , BN and mica that rarely reacts with Zr, Ti or Cr in a metal matrix. It was found that the purpose can be sufficiently attained by applying this to the metal or alloy used for the mold material by electroless plating, electrolytic plating or spray coating. After the coating, the surface is polished preferably with an emery paper of about No. 1000.

[0052] The content of the self-lubricant in the composite material (cermet) to be plated or sprayed is not particularly limited. However, although the reaction resistance and the lubricating property are improved, an increased content of the self-lubricant causes deterioration of the peeling resistance of the film, then the content is preferably set to about 10 to 30 vol. %.

[0053] The metal in the composite material to be coated by plating is not particularly limited, and any metal or alloy can be used. Particularly, use of a metal or an alloy having a high melting point and high thermal conductivity is preferred, for example, a Cu alloy, stainless steel, a Ni alloy, a Co alloy and a W alloy.

[0054] In the continuous casting of a Cu alloy by the intermittent pulling out method by the use of this mold, a further profound effect can be obtained by adapting either or both of measures of (1) giving a vibration that has a frequency larger than the intermittent cycle by two orders or more and that has a component vertical to the pulling out direction to

the mold and (2) continuously supplying a lubricant or an anti-sticking material between an inner wall of the mold and the slab.

[0055] According to the intermittent pulling out method, since the frictional resistance between the inner wall of the mold and the slab is reduced in terms of lubricating effect, a sufficiently sound slab can be continuously, efficiently and safely produced.

[0056] If a vibration that has a frequency larger than the intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction is given to the mold, the similar effect can be obtained over a longer time. An increased vibration frequency is more preferable, and the frequency is preferably set to 5000 cpm (83 Hz) or more, and more preferably to 60000 cpm (1 kHz) or more, which is close to the ultrasonic area.

[0057] The lubricant to be supplied between the inner wall of the mold and the slab is the same as described above.

[0058] (C) A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which the self-lubricant or the metal-based self-lubricating composite member is used at least for the inner wall in the solidification starting position of the Cu alloy melt:

[0059] Figure 3 is a schematic view of a continuous casting mold for a Cu alloy as an example of the continuous casting mold according to the present invention. This is an example of the mold that is composed of a combination of plurality of parts, that is, the mold composed of a part of mold member 3 including an inner wall in the solidification starting position 10 of the Cu alloy melt, and another part of mold member 3'. The self-lubricant or the metal-based self-lubricating composite member is used for the part of mold member 3 including the inner wall in the solidification starting position 10 of the Cu alloy melt, and any one member selected from the graphite, the ceramic and the metal member is used for the other part of mold member 3'.

[0060] The mold composed of a plurality of parts, that is, the mold composed of a combination of a part of mold member including an inner wall in the solidification starting position, using a self-lubricant or a metal-based self-lubricating composite material, and another part of mold member using any one of the selected from a self lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal material, leads to a sound slab which can be continuously, efficiently and stably produced.

[0061] And a continuous casting method of a Cu alloy ensuring excellent characteristics such as strength, electric conductivity, bending workability and fatigue strength of a final product after working and heat treatment can be provided. Particularly, in application to casting of a Cu alloy containing elements such as Zr, Ti, Cr, Ta and V that easily form into carbides, a profound effect can be obtained.

[0062] As the part of mold member including the inner wall, any of a glassy carbon, a layered carbon, a BN (example 22), and a metal-based self-lubricating composite member obtained by dispersing and mixing a self-lubricant such as MoS₂, WS₂, BN, or mica that rarely reacts with Zr, Ti or Cr in a metal matrix can be selected. The graphite, the ceramic and the metal members to be used for the other part of mold member are the same as described above.

[0063] (D) A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material:

[0064] Figure 4 is a schematic view of a continuous casting mold for a Cu alloy as one example of the continuous casting mold according to the present invention, which is composed of a plurality of parts of members, and which has a coating 8 of a self-lubricant or a metal-based self-lubricating composite material applied to the inner wall of the mold in the solidification starting position 10 of the Cu alloy melt. The mold is composed of a part of mold member 3 and another part of mold member 3', using two kinds of parts of members selected from a metal-based self-lubricating composite, a graphite, a ceramic and a metal member.

[0065] The mold, which is composed of a part of any one member of mold selected from a graphite, a ceramic and a metal member, and another downstream part of a metal-based self-lubricating composite or a graphite member, has a coating of the self-lubricant or the metal-based self-lubricating composite material applied to the inner wall in the solidification starting position of a Cu alloy melt. The mold leads to a sound slab that can be continuously, efficiently and stably produced. And a continuous casting method of the Cu alloy ensuring excellent characteristics such as strength, electric conductivity, bending workability and fatigue strength of the final product after working and heat treatment, can be provided. Particularly, in application to a Cu alloy containing elements such as Zr, Ti, Cr, Ta and V that easily form into carbides, a profound effect can be obtained.

[0066] The graphite member, the ceramic member, the metal member, and the metal-based self-lubricating composite member to be used for the mold member are the same as described above. As for the coating to the inner wall of the mold, any of the glassy carbon, the layered carbon, and the BN which are self-lubricants and the metal-based self-lubricating composite member obtained by dispersing and mixing self-lubricants such as MoS₂, WS₂, BN and mica, that rarely react with Zr, Ti or Cr in a metal matrix, can be selected.

[0067] (E) The continuous casting mold for a Cu alloy according to any one of (A) to (D) above, wherein the inner wall

in the position that contacts with the Cu alloy melt is coated with a ceramic material:

[0068] Another example of the continuous casting mold according to the present invention, is shown in Fig. 5. In this continuous casting mold for a Cu alloy, the mold member 3 including a mold portion in the solidification starting position 10 of the Cu alloy melt, is composed of a metal-based self-lubricating composite, and a coating 9 of a ceramic material is applied to the inner wall in the position that contacts with the Cu alloy melt in order to suppress the reaction with the melt. The coating method of the ceramic can be applied by spraying, CVD, etc.

[0069] The other example of the continuous casting mold according to the present invention, is shown in Fig. 6. This continuous casting mold for a Cu alloy is composed of a metal member for the mold member 3, in which a coating 8 of the metal-based self-lubricating composite material is applied to the inner wall in the solidification starting position 10 of the Cu alloy melt, and a coating 9 of the ceramic is applied to the inner wall in the position of the mold that contacts with the Cu alloy melt in order to suppress the reaction with the melt. The coating method of the ceramic is the same as described above.

[0070] Another example of the continuous casting mold according to the present invention is further, shown in Fig. 7. This continuous casting mold for a Cu alloy is composed of an upstream part of mold of a metal member and another downstream part of mold of a graphite member. The part of mold of a metal member has a coating 8 of a metal-based self-lubricating composite material applied to the inner wall in the solidification starting position 10 of the Cu alloy melt, and has a coating 9 of a ceramic material applied to the inner wall in the position of the mold that contacts with the Cu alloy melt in order to suppress the reaction with the melt. The coating method of the ceramic is the same as described above.

[0071] As described in Figs. 5 to 7, when the part of mold is composed of the metal or metal-based self-lubricating composite member, it is further effective to apply the coating of the ceramic to the inner wall in the position of the mold that contacts with the Cu alloy melt in order to avoid the reaction of the member with Zr, Ti, Cr and so on in the melt. From the point of peeling resistance, it is recommended as the coating method of ceramics to apply a coating of a cushioning material about 50 μm thick (e.g., Ni plating, frame-coating of WC-27 wt% NiCr, and so on), and then apply a ceramic coating about 200 μm thick thereon by frame coating. From the point of reaction resistance, a ceramic composed of a further stable oxide, at a casting temperature of the Cu alloy of 1250°C, is preferred. For example, ZrO_2 -8 wt% Y_2O_3 , ZrO_2 -25 wt% MgO , ZrO_2 -5 wt% CaO and so on are recommended since no adhesion of the Cu alloy is caused. More preferably, the inner wall in the position of the upstream part of mold to be coated is preliminarily ground so as not to form a difference in level after ceramic coating.

<Cu Alloys to Apply the Present Invention>

[0072] A profound effect can be obtained to any alloy when applying the inventive method. It is the most effective to apply Cu alloys including Cu-Ti-X alloys (X: Cr, Fe, Co, Ta, Nb, Mo, V, Mn, Be, Si, Ni, Sn, Ag, etc.), Cu-Zr-X alloys (X: Cr, Fe, Co, Ta, Nb, Mo, V, Mn, Be, Si, Ni, Sn, Ag, etc.), and Cu-Ti-Zr alloys.. Some compounds such as Ti-Cr and Zr-Cr and some metals such as Ti, Zr and Cr precipitates in a certain high-temperature region in the cooling process after solidification, which is apparent from the phase diagrams of Ti-Cr, Zr-Cr and Ti-Zr binary alloy systems shown in Figs. 8, 9 and 10. These precipitates formed in a certain high-temperature region in the cooling process after solidification tend to be coarsened or aggregated, and it is quite difficult to dissolve them by the subsequent solution treatment, which is apparent from the phase diagrams.

[0073] A slab or bloom, according to the present invention, has a profound effect through the process of working such as rolling at 600°C or lower and an aging treatment in the temperature region of 150 to 750°C, without a hot process such as hot rolling and solution treatment described in the above-mentioned Patent Document 1. The alloy is strengthened by a fine precipitation of an intermetallic compound between Cu and an alloy element such as Cu_4Ti and Zr_9Cu_2 or between the alloy elements, or a fine metal precipitate of Ti, Zr, Cr and so on. Then, it is enhanced in electric conductivity by the resulting reduction of the dissolved elements such as Ti, Zr, and Cr that are harmful to electric conductivity. If a coarsened or agglomerate precipitate is present before the aging treatment in the final process, sufficient precipitation hardening cannot be attained. The presence of such coarse particles deteriorates the bending workability, fatigue characteristic and impact resistance of the final product.

[0074] Since it is almost impossible to dissolve the coarsened or agglomerate compounds formed in the cooling process after solidification, increasing the cooling rate is necessary in order to prevent the precipitation. The average cooling rate from the temperature of the start of solidification to 600°C is preferably 1°C/s or more, and further preferably 10°C/s or more.

[0075] A Cu alloys according to the present invention include the Cu alloy containing, by mass%, one or more components selected from Cr: 0.01 to 5%, Ti: 0.01 to 5%, Zr: 0.01 to 5%, Nb: 0.01 to 5%, Ta: 0.01 to 5%, Al: 0.01 to 5%, Mo: 0.01 to 5%, V: 0.01 to 5%, Co: 0.01 to 5%, Mn: 0.01 to 5%, Si: 0.01 to 5%, Be: 0.01 to 5%, and Hf: 0.01 to 5%.

[0076] Further, a Cu alloy containing, in addition to the above components, by mass%, 0.001 to 5 mass% in total of one or more of the alloy components selected from at least one group of the following three groups is given:

First group: 0.001 to 1 mass% in total of one or more selected from P, B, Sb, Bi, Pb, Cd, S and As;

Second group: 0.01 to 5 mass% in total of one or more selected from Sn, Ag, Zn, Ni, Au, Pd, Fe, W, In and Ge; and

Third group: 0.01 to 3 mass% in total of one or more selected from Te, Se, Sr, Tl, Rb, Cs, Ba, Re, Os, Rh, Po, Ga, Tc, Ru, Pd, Ir, Pt and Ta.

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[0077] A Cu alloy further containing 0.001 to 2 mass% in total of one or more alloy components selected from Li, Ca, Mg and rare earth elements is also given. The rare earth elements include Sc, Y and lanthanide, and each element may be added alone as raw material or in a form of mish metal.

10 <Method for Producing Cu alloy of the Present Invention>

[0078] Prior to continuous casting using the mold according to the present invention, a Cu alloy with given chemical composition is prepared by a melting furnace. The melting is desirably performed under a non-oxidizing atmosphere. While the melting is inevitably performed in the air, it is effective to suppress the oxidation by shrouding the melt by a flux (e.g., cryolite, fluorite, etc.) or charcoal particles. The melt is poured into a holding furnace. The melting is desirably conducted using the holding furnace in order to suppress the oxidation during the pouring.

[0079] Any of horizontal type, vertical type and so on can be adapted to this continuous casting if it is the direct-connection type of continuous casting using the mold directly connected to a holding furnace.

The mold according to the present invention has minimized operational problems in the production of the Cu alloy according to the present invention because of the low reactivity with the melt and a satisfactory lubricating property. However, since the inner wall in the vicinity of the solidification starting position in the mold is gradually thinned by the reaction with the melt or abrasion, the slab might be caught thereby and not easily pulled out. In such a case, it is effective to uniformly thin the inner wall by adjusting the cooling condition of the mold, the pulling out rate, or the like and moving the solidification position.

25 In general, the slab is intermittently pulled out. There are various patterns: (A) pull-stop pattern, (B) pull-pushback pattern, (C) pull-stop-pushback pattern and (D) pull-stop-pushback-stop pattern, any of which can be adapted. The higher cooling rate in the cooling process after solidification is desirable based on the above-mentioned reason. Particularly, it is desirable to take measure to raise the cooling rate in the secondary cooling zone corresponding to the temperature range of coarsened or agglomerated precipitation. Specifically, it is effective to employ water spray, air spray, or air-water mixed spray just after leaving the mold

30 **[0080]** Thereafter, the final product is obtained by a combination of working such as rolling at 600°C or lower and the aging treatment at 150 to 750°C. This working may be performed, of course, in the cooling process after continuous casting.

35 <Example A>

[0081] Cu alloys containing 2.0 ± 0.1 wt% of Ti, 1.0 ± 0.1 wt% of Cr, 0.4 ± 0.02 wt% of Sn, and 0.1 ± 0.01 wt% of Zn were melted in a high frequency vacuum melting furnace, and a continuous casting test was carried out in 37 kinds of various production methods shown in Tables 1 and 2. Each Cu alloy melt was transferred to a holding furnace, and a slab of 20 mmx200mm section was intermittently pulled out in a predetermined condition while holding the temperature of the furnace at 1250°C. As a refractory of the melting furnace and the holding furnace, graphite was used. The oxidation of the melt was suppressed by an Ar gas flow during pouring in addition to charcoal covering. In each test, a water-cooled jacket composed of the Cu alloy was located adjacent to the mold in order to perform primary cooling, and the slab leaving the mold was cooled again by an air-water mixed spray. The temperature measurement was performed basically after leaving the mold by use of a thermocouple or radiation thermometer. In some cases, the mold temperature was measured by boring a through-hole from the mold outer wall to a position 5 mm inside and inserting the thermocouple. Using both the measured data and the physical properties of each mold material, whereby the solidification starting position was estimated, performed a heat transfer analysis. The average cooling rate from the solidification start point to 600°C was calculated based on the above data. In the tests shown in Tables 1 and 2, the cooling rate was controlled to the range of 5 ± 2 °C.

50 **[0082]** [Table 1]

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Table 1

Test No.	Mold	Vertical vibration of mold	Forced lubrication of mold	Average casting speed (mm/min)	Casting length (m)	Quality of slab surface
1 The Present Invention, Fig. 1	Mold composed of a graphite member with bulk density of 1.99.	Non	Non	258	60m Complete casting	Satisfactory
2 The Present Invention, Fig. 1	Mold composed of a glassy carbon member.	Non	Non	258	60m Complete casting	Excellent
3 The Present Invention, Fig. 1	Mold composed of a metal-based self-lubricating composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy followed by sintering.	Non	Non	258	60m Complete casting	Satisfactory
4 The Present Invention, Fig. 1	Mold composed of a bulk density graphite member with bulk density of 1.99.	Frequency 5kHz Amplitude 5μm	Non	258	60m Complete casting	Satisfactory
5 The Present Invention, Fig. 1	Mold composed of a bulk density graphite member with bulk density of 1.99.	MoS ₂ fine particle + Mineral oil	Non	258	60m Complete casting	Satisfactory
6 The Present Invention, Fig. 1	Mold composed of a bulk density graphite member with bulk density of 1.99.	MoS ₂ fine particle + Mineral oil	Frequency 5kHz Amplitude 5μm	258	60m Complete casting	Satisfactory

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7	The Present Invention, Fig. 1	Mold composed of a metal-based composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy followed by sintering.	Frequency 5kHz Amplitude 5μm	Non	258	60m Complete casting	Satisfactory	
8	The Present Invention, Fig. 1	Mold composed of a metal-based composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy followed by sintering.	MoS ₂ fine particle +Mineral oil	Non	258	60m Complete casting	Satisfactory	
9	The Present Invention, Fig. 1	Mold composed of a metal-based composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy followed by sintering.	Frequency 5kHz Amplitude 5μm	MoS ₂ fine particle +Mineral oil	Non	258	60m Complete casting	Satisfactory
10	The Present Invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.82 with coating of a glassy carbon material applied to the inner wall.	Non	Non	258	60m Complete casting	Excellent	
11	The Present Invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.82 with coating of a layered carbon material applied to the inner wall.	Non	Non	258	60m Complete casting	Satisfactory	
12	The Present Invention, Fig. 2	Mold composed of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%) with coating of BN applied to the inner wall by CVD.	Non	Non	258	60m Complete casting	Satisfactory	
13	The Present Invention, Fig. 2	Mold composed of a W alloy member with coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy, applied to the inner wall by plating.	Non	Non	258	60m Complete casting	Satisfactory	

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			Frequency 5kHz	Amplitude 5µm	Non	258	60m Complete casting	Satisfactory
14	The Present Invention, Fig. 2	Mold composed of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%), with coating of BN applied to the inner wall by CVD.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory
15	The Present Invention, Fig. 2	Mold composed of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%), with coating of BN applied to the inner wall by CVD.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory
16	The Present Invention, Fig. 2	Mold composed of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%), with coating of BN applied to the inner wall by CVD.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory
17	The Present Invention, Fig. 2	Mold composed of a W alloy member, with coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy, applied to the inner wall by plating.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory
18	The Present Invention, Fig. 2	Mold composed of a W alloy member, with coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy, applied to the inner wall by plating.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory
19	The Present Invention, Fig. 2	Mold composed of a W alloy member, with coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy, applied to the inner wall by plating.	MoS ₂ fine particle + Mineral oil	258	Non	258	60m Complete casting	Satisfactory

[0083] [Table 2]

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Table 2

No.	Mold	Vertical vibration mold	Forced lubrication of mold	Average casting speed (mm/min)	Casting length (m)	Quality of slab surface
20 The Present Invention, Fig. 3	Mold composed of a combination of a part of a glassy carbon member including the inner wall in the solidification starting position and another part of a graphite member with bulk density of 1.82.	Non	Non	258	60m Complete casting	Excellent
21 The Present Invention, Fig. 3	Mold composed of a combination of a part of a layered carbon member including the inner wall in the solidification starting position and another part of a graphite member with bulk density of 1.82.	Non	Non	258	60m Complete casting	Satisfactory
22 The Present Invention, Fig. 3	Mold composed of a combination of a part of a BN member including the inner wall in the solidification starting position and another part of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%).	Non	Non	258	60m Complete casting	Satisfactory
23 The Present Invention, Fig. 3	Mold composed of a combination of a part of a metal-based self-lubricating composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy, including the inner wall in the solidification starting position, and another part of a Cu-Cr alloy member.	Non	Non	258	60m Complete casting	Satisfactory
24 The Present Invention, Fig. 4	Mold composed of a combination of an upper stream part of a graphite member with bulk density of 1.82 with a coating of a glassy carbon material, and another down stream part of a metal-based self-lubricating composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy.	Non	Non	258	60m Complete casting	Excellent

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				60m Complete casting		
25	The Present Invention, Fig. 4	Mold composed of a combination of an upper stream part of a graphite member with bulk density of 1.82 with a coating of a layered carbon material, and another down stream part of a metal-based self-lubricating composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy.	Non	Non	258	Satisfactory
26	The Present Invention, Fig. 4	Mold composed of a combination of a part of a ceramic member obtained by sintering sialone (30vol%) and BN (70vol%) with a CVD coating of BN, and another part of a graphite member with bulk density of 1.82.	Non	Non	258	Satisfactory
27	The Present Invention, Fig. 4	Mold composed of a combination of a part of a W alloy member obtained by dispersing WS ₂ +BN to W alloy with a plate coating of a metal-based self-lubricating composite material, and another part of a graphite member with bulk density of 1.82.	Non	Non	258	Satisfactory
28	The Present Invention, Fig. 5	Mold composed of a metal-based self-lubricating composite member obtained by dispersing WS ₂ +BN (85vol%) to W alloy followed by sintering with a frame coating of ZrO ₂ 8wt% Y ₂ O ₃ applied to the inner wall in the upper stream position including the solidification starting position.	Non	Non	258	Satisfactory
29	The Present Invention, Fig. 6	Mold composed of a W alloy member with a plate coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy applied to the inner wall in the solidification starting position and with a sprayed ZrO ₂ 8 wt% Y ₂ O ₃ applied to the inner wall in the upper stream position including the solidification starting position.	Non	Non	258	Satisfactory

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30	The Present Invention, Fig. 7	Mold composed of a combination of an upstream part of a W alloy member with a plate coating of a metal-based self-lubricating composite material obtained by dispersing WS ₂ +BN to W alloy applied to the inner wall in the solidification starting position, and with a sprayed ZrO ₂ ·8wt% Y ₂ O ₃ applied to the inner wall in the upper stream position including the solidification starting position, and a downstream part of a graphite member with bulk density of 1.83.	Non	258	60m Complete casting	Satisfactory
31	The Present Invention, Fig. 1	Mold composed of a high-bulk density graphite member with bulk density of 1.85.	Frequency 5kHz Amplitude 5µm	Non	258	60m Complete casting
32	The Present Invention, Fig. 1	Mold composed of a high-bulk density graphite member with bulk density of 1.85.	MoS ₂ fine particle +Mineral oil	258	60m Complete casting	Satisfactory
33	The Present Invention, Fig. 1	Mold composed of a high-bulk density graphite member with bulk density of 1.82.	Frequency 5kHz Amplitude 5µm	MoS ₂ fine particle +Mineral oil	258	60m Complete casting
34	Comparative	Mold composed of a natural graphite member.	Non	Non	258	3m Interrupt of pulling out due to slab failure
35	Comparative	Mold composed of a graphite member with bulk density of 1.77.	Non	Non	258	3m Interrupt of pulling out due to slab failure

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36	Comparative	Mold composed of graphite member with bulk density of 1.82.	Non	Non	258	4m Interrupt of pulling out due to slab failure Frequent occurrence of pulling out mark crack
37	Comparative	Mold composed of a graphite member with bulk density of 1.90.	Non	Non	258	8m Interrupt of pulling out due to slab failure Frequent occurrence of pulling out mark crack

[0084] The casting was intended to ensure a length of about 60 m upon completion. However, due to an abnormal rise of pulling out resistance because of mold biting in the initial solidification shell was observed in some cases in the middle of the pulling out. The quality of the slab surface was evaluated by visually determining flaws thereon. It is apparent from Tables 1 and 2 that the complete casting was successful in the present invention with good quality. 5 However, in the comparative, complete casting could not be performed and the quality was not acceptable to commercial work.

<Example B>

10 [0085] There are 34 kinds of Cu alloys of the chemical compositions shown in Table 3, which were smelted similarly to Example A. A continuous casting test was carried out while varying the production condition, and they were evaluated in the same method as Example A. The results are shown in Tables 4 and 5. A satisfactory result was obtained in any mold, any casting condition and any chemical composition in the present invention. In contrast, an unsatisfactory result for quality was obtained using comparative molds.

15 [0086] [Table 3]

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Alloy No.	Ti	Cr	Zr	Ag	Sn	Mn	Co	Si	Mg	Fe	Al	Zn	Ni	P	Others
1	-	0.39	2.95	-	-	-	-	-	-	-	-	-	-	-	-
2	2.01	0.40	-	0.25	-	-	-	-	-	-	-	-	-	-	Mg:0.1, Ca:0.1
3	1.02	.20	0.99	-	-	-	-	-	-	-	-	-	-	-	-
4	2.99	1.01	-	-	-	-	-	-	-	-	-	-	-	-	-
5	-	0.99	3.99	-	-	-	-	-	-	-	-	-	-	-	-
6	-	2.00	0.12	-	-	-	-	-	-	-	-	-	-	-	Li:0.1, Sc:0.5
7	0.98	1.97	-	5.00	-	-	-	-	-	-	-	-	-	-	-
8	3.01	-	2.01	-	-	-	-	-	-	-	-	-	-	-	-
9	1.01	4.00	-	0.10	-	-	-	-	-	-	-	-	-	-	-
10	5.00	0.99	-	-	-	-	-	-	-	-	-	-	-	0.001	Nb:0.2, Ge:2.0
11	3.01	0.97	-	-	0.41	-	-	0.49	-	-	0.51	-	-	-	Hf:1.0, Bi:0.5
12	-	0.98	1.99	-	0.10	-	-	0.20	1.00	-	-	0.21	-	-	-
13	1.98	0.99	-	-	0.35	-	-	0.04	-	-	0.29	-	1.500	.001	Sb:1.1
14	0.50	0.99	0.05	-	-	-	-	-	-	2.00	0.21	0.50	-	0.001	-
15	2.02	1.01	0.49	-	2.01	-	-	-	-	0.51	-	0.26	0.01	0.120	-
16	3.01	-	0.72	0.01	0.29	-	-	0.41	-	0.32	-	0.01	-	-	Ta:0.5, Se:0.2
17	1.98	0.99	-	-	0.39	-	-	-	-	-	-	0.40	-	-	-
18	-	1.03	1.93	-	1.01	-	-	0.01	-	0.01	-	-	--	0.150	-
19	1.95	1.01	-	-	0.35	-	0.20	-	-	-	0.21	1.01	-	-	Mo:0.3, W:0.05
20	-	1.01	2.00	-	0.40	0.01	0.01	0.11	-	-	0.15	-	-	-	-
21	1.98	0.50	-	-	0.19	-	0.33	0.48	0.01	-	-	0.01	0.05	-	Y:1.8, Nd0.8, Ce0.4
22	4.01	0.98	-	-	-	-	0.19	0.31	-	-	-	0.21	0.45	-	-
23	2.02		0.29	-	-	-	2.00	0.45	-	-	-	0.11	0.11	-	-
24	1.99		0.99	0.52	-	-	-	0.39	-	-	-	-	0.81	-	V:0.5, In:1.2
25	1.98	1.01	-	-	-	0.01	-	0.05	-	-	0.01	-	-	-	-

55	50	45	40	35	30	25	20	15	10	5
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(continued)

Alloy No.	Ti	Cr	Zr	Ag	Sn	Mn	Co	Si	Mg	Fe	Al	Zn	Ni	P	Others
26	-	0.98	2.01	0.25	-	0.50	-	0.79	-	0.01-	-	0.46	-	-	-
27	2.02	-	0.98	-	-	0.55	0.39	2.00	-	-	-	-	-	-	Te:0.4, Sr:3.2, B:0.5
28	3.01	1.03	-	-	-	2.00	-	0.50	-	0.01	-	-	-	-	-
29	-	1.02	2.02	-	-	-	1.00	0.20	-	0.20	0.09	-	0.15	-	-
30	1.99	3.03	-	-	0.01	-	0.48	-	-	-	2.00	-	0.35	-	B:0.01, Nb2.0
31	3.99	0.10	3.00	-	-	-	-	0.10	0.05	-	-	-	-	-	-
32	1.99	1.00	-	-	-	-	-	-	-	-	-	3.00	-	0.003	-
33	-	0.98	5.00	2.00	-	-	-	-	-	-	-	-	3.00	-	Gd:1.0, Mm:2.0
34	2.01	1.02	1.01	-	-	-	-	0.11	-	0.10	-	-	-	-	B:1.0

[0087] [Table 4]

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Table 4

Test No.	Alloy No.	Mold	Vertical vibration of mold	Forced lubrication of mold	Average casting speed(mm/min)	Casting length (m)	Quality of slab
38	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
39	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
40	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
41	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
42	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
43	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent

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				Non	Non	258	60m Complete casting	Excellent
44	The present invention, Fig. 2	7	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
45	The present invention, Fig. 2	8	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
46	The present invention, Fig. 2	9	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
47	The present invention, Fig. 2	10	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
48	The present invention, Fig. 2	11	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
49	The present invention, Fig. 2	12	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
50	The present invention, Fig. 2	13	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
51	The present invention, Fig. 2	14	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent

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				Non	258	60m Complete casting	Excellent
52	The present invention, Fig. 2	15	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
53	The present invention, Fig. 2	16	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
54	The present invention, Fig. 2	17	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
55	The present invention, Fig. 2	18	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
56	The present invention, Fig. 2	19	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
57	The present invention, Fig. 2	20	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent
58	The present invention, Fig. 2	21	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	60m Complete casting	Excellent

[0088] [Table 5]

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Table 5

No.	Alloy No.	Mold	Vertical vibration of mold	Forced lubrication of mold	Average casting speed (mm/min)	Casting length (m)	Quality of slab
59	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
60	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
61	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
62	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
63	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
64	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
65	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
66	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
67	The present invention, Fig. 2	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent

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68	The present invention, Fig. 2	31	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
69	The present invention, Fig. 2	32	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
70	The present invention, Fig. 2	33	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
71	The present invention, Fig. 2	34	Mold composed of a graphite member with bulk density of 1.83, with a coating of a glassy carbon material applied to the inner wall in the solidification starting position.	Non	Non	258	60m Complete casting	Excellent
72	The present invention, Fig. 1	3	Mold composed of a graphite member with bulk density of 1.99.	Non	Non	258	60m Complete casting	Satisfactory
73	The present invention, Fig. 3	3	Mold composed of a combination of a part of a glassy carbon member including the solidification starting position, and another part of a graphite member with bulk density of 1.83.	Non	Non	258	60m Complete casting	Excellent
74	The present invention, Fig. 3	3	Mold composed of a combination of a part of a layered carbon member including the solidification starting position, and another part of a graphite member with bulk density of 1.83.	Non	Non	258	60m Complete casting	Satisfactory
75	Comparative	3	Mold composed of a graphite member with bulk density 1.82.	Non	Non	258	4m Interrupt of pulling out due to slab failure	Frequent occurrence of pulling out mark crack
76	Comparative	4	Mold composed of a graphite member with bulk density 1.82.	Non	Non	258	4m Interrupt of pulling out due to slab failure	Frequent occurrence of pulling out mark crack
77	Comparative	11	Mold composed of a graphite member with bulk density 1.82.	Non	Non	258	4m Interrupt	Frequent occurrence of pulling

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55	78	Comparative	12	Mold composed of a graphite member with bulk density 1.82.	Non	258	4m Interrupt of pulling out due to slab failure Frequent occurrence of pulling out mark crack

<Example C>

[0089] For the three kinds of alloys shown in Table 6, slabs of 20 mm×200mm section were casted by use of a mold composed of graphite with bulk density of 1.82, with a glassy carbon applied to the inner wall, and the influence of the cooling rate on characteristics was examined by varying the water quantities of primary cooling and secondary cooling, and varying the cooling rate from the solidification start point to 600°C. The cooled slabs were cold rolled to 3 mm, then aged at 400°C for 2hr under an inert gas atmosphere followed by cold rolling to 0.5 mm, and finally aged at 350°C for 6 hr. The electric conductivity and tensile strength by tensile test of the resulting test materials were evaluated by the following methods.

[0090] [Table 6]

Table 6

	Alloy No.	Ti	Cr	Zr	Cooling rate (°C/s)	TS(MPa)	IACS(%)	Evaluation*	Remarks
Comparative	35	2.00	1.51	-	0.10	-	-	×	Not evaluated because of cracking during cold rolling
The present invention	35	2.01	1.51	-	0.50	802	40	O	
	35	1.98	1.49	-	5.00	956	27	O	
	35	1.99	1.51	-	10.00	1174	19	O	
Comparative	36	-	1.50	2.02	0.10	420	65	×	
The present invention	36	-	1.50	2.04	0.50	750	52	O	
	36	-	1.49	1.99	5.00	872	48	O	
	36	-	1.48	2.00	10.00	1012	35	O	
Comparative	37	1.51	-	1.49	0.10	-	-	×	Not evaluated because of cracking during cold rolling
The present invention	37	1.53	-	1.50	0.50	892	35	O	
	37	1.49	-	1.49	5.00	1015	24	O	
	37	1.52	-	1.48	10.00	1230	17	O	

Note: * O means satisfying equation (1)

<Tensile Strength>

[0091] A test piece 13 B, according to the regulation of JIS Z 2201, was collected from each specimen, and the tensile strength [TS (MPa)] at room temperature (25°C) was determined according to the method regulated in JIS Z 2241.

<Electric Conductivity>

[0092] A test piece with width of 10mm × length of 60 mm was prepared from each specimen, current was carried in

the longitudinal direction of the test piece in order to measure the potential difference between both ends of the test piece, and the electric resistance was determined by a 4-terminal method. Successively, the electric resistance (resistivity) per unit volume was calculated from the volume of the test piece that was measured by a micrometer, and the electric conductivity [IACS (%)] was determined from its ratio to resistivity $1.72 \mu\Omega\text{cm}$ of a reference sample obtained by annealing polycrystalline pure copper.

[0093] In case of having a cooling rate lower than 0.5°C/s according to the comparative, cracking was caused in cold rolling, and even if cold rolling could be performed, the balance between strength and electric conductivity was poor. On the other hand, the balance between both was satisfactory and the high tensile strength in relation with the high electric conductivity is provided according to the present invention,

[0094] The "high tensile strength in relation with conductivity" means a state satisfying the following equation (1) (this state is hereinafter referred to as "well-balanced state of tensile strength and electric conductivity"):

$$TS \geq k_{10} + k_{11} \cdot \exp(-k_{12} \cdot IACS) \dots \quad (1)$$

wherein TS: tensile strength (MPa), IACS: electric conductivity (%), $k_{10}=658.06$, $k_{11}=985.48$, and $k_{12}=0.0513$. IACS means the percentage to the electric conductivity of the pure copper polycrystalline material.

[0095] Further, characteristics of the alloys shown in Table 3 were similarly evaluated in the above-mentioned casting condition while setting the cooling rate 5°C/s from the solidification start to 600°C . The result is shown in Table 7. As a result, each alloy has the balance between strength and conductivity satisfying the above equation (1), and a satisfactory result was obtained by the present invention.

[0096] [Table 7]

Table 7

Alloy No.	TS(MPa)	IACS(%)
1	800	45
2	1145	25
3	967	32
4	1281	20
5	820	45
6	668	79
7	965	36
8	1279	19
9	970	40
10	1469	8
11	1286	15
12	960	33
13	1143	21
14	862	36
15	1139	20
16	1288	14
17	1145	18
18	980	28
19	1138	21
20	965	29
21	1135	19

(continued)

Alloy No.	TS(MPa)	IACS(%)
22	1386	9
23	1140	17
24	1152	18
25	1142	16
26	972	33
27	1141	20
28	1279	15
29	992	28
30	1137	20
31	1385	14
32	1145	19
33	1002	30
34	1149	18

[Industrial Applicability]

[0097] The present invention involves a continuous casting mold used mainly for a direct-connection type of continuous casting, with a mold directly connected to a holding furnace, and a continuous casting method of a Cu alloy. Namely, the present invention provides a mold capable of continuously and efficiently producing a sound slab or bloom, and also a continuous casting method of a Cu alloy which ensures excellent characteristics, such as strength, electric conductivity, vending workability, impact resistance and fatigue strength of the final product after working and heat treatment. Particularly, the application of the production of the Cu alloy containing elements such as Zr, Ti, Cr, Ta and V that easily generate carbides provides a profound effect.

[Brief Description of the Figures]

[0098]

[Fig. 1] An example of a continuous casting mold according to the present invention.

[Fig. 2] An example of the continuous casting mold according to the present invention, which has a coating 8 of a self-lubricant or a metal-based self-lubricating composite material applied to the mold inner wall in the solidification starting position of a Cu alloy melt.

[Fig. 3] An example of the continuous casting mold according to the present invention, which is composed of a plurality of parts of mold members.

[Fig. 4] An example of the continuous casting mold according to the present invention, which is composed of a plurality of parts of mold members, and has a coating 8 of a self-lubricant or metal-based self-lubricating composite material applied to the mold inner wall in the solidification starting position of an alloy melt.

[Fig. 5] Another example of the continuous casting mold according to the present invention, which includes a coating 9 of ceramic material applied to the inner wall in the position that contacts with a Cu alloy melt in order to inhibit the reaction with the melt.

[Fig. 6] Another example of the continuous casting mold according to the present invention, which has a coating 8 of a metal-based self-lubricating composite material applied to the mold inner wall in the solidification starting position of an alloy melt, and a coating 9 of a ceramic material applied to the inner wall in the position that contacts with a Cu alloy melt in order to inhibit reaction with the melt.

[Fig. 7] Another example of the continuous casting mold according to the present invention, which is composed of an upstream part of a metal member and a downstream part of a graphite member, with a coating 8 of a metal-based self-lubricating composite material applied to the inner wall in the solidification starting position of an alloy melt, and with a coating 9 of a ceramic material applied to the inner wall in the position that contacts with a Cu alloy melt in order to inhibit the reaction with the melt.

[Fig. 8] A phase diagram of a Ti-Cr alloy.
 [Fig. 9] A phase diagram of a Zr-Cr alloy.
 [Fig. 10] A phase diagram of a Ti-Zr alloy.

5 [Explanation of Reference Numerals]

[0099]

10 1. Cu alloy melt
 2. Holding furnace wall
 3. Mold member
 3. Another part of mold member
 4 Slab
 5. Cooling jacket
 15 6. Secondary cooling
 7. Pulling out direction
 8. Coating to the inner wall in the solidification starting position of a Cu alloy melt
 9. Coating to the inner wall on the position that contacts with a Cu alloy melt
 10. Solidification starting position of a Cu alloy melt

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Claims

25 1. A continuous casting mold for a Cu alloy, using any one member selected from a glassy carbon, a metal-based self-lubricating composite or a graphite with a bulk density exceeding 1.92, at least for the mold member including the solidification starting position of the Cu alloy melt.

30 2. A continuous casting mold for a Cu alloy, composed of any one member selected from a graphite, a ceramic and a metal member or of a combination of two or more parts of members thereof, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material.

35 3. A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which the self-lubricant or the metal-based self-lubricating composite member is used at least for the inner wall in the solidification starting position of the Cu alloy melt.

40 4. A continuous casting mold for a Cu alloy, composed of a combination of two or more parts of members selected from a self-lubricant, a metal-based self-lubricating composite, a graphite, a ceramic and a metal member, in which at least the inner wall in the solidification starting position of the Cu alloy melt is coated with a self-lubricant or a metal-based self-lubricating composite material.

45 5. The continuous casting mold for a Cu alloy according to any one of claims 1 to 4, wherein the inner wall in the position that contacts with the Cu alloy melt is coated with a ceramic material.

6. A continuous casting method of a Cu alloy, comprised of performing continuous casting by a slab intermittent pulling out method by use of the mold according to any one of claims 1 to 5.

50 7. A continuous casting method of a Cu alloy, comprised of giving, at the time of continuously casting a Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the slab intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction of the slab.

8. A continuous casting method of a Cu alloy, comprised of continuously supplying, at the time of the continuously casting the Cu alloy by an intermittent pulling out method, a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

55 9. A continuous casting method of a Cu alloy, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the slab intermittent pulling out

frequency by two orders or more and that has a component vertical to the pulling out direction to a mold, and continuously supplying a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

5 10. The continuous casting method of a Cu alloy according to claim 6, comprised of giving, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a vibration that has a frequency larger than the intermittent pulling out frequency by two orders or more and that has a component vertical to the pulling out direction of the slab.

10 11. The continuous casting method of a Cu alloy according to claim 6 or 10, comprised of continuously supplying, at the time of continuously casting the Cu alloy by an intermittent pulling out method, a lubricant or an anti-sticking material between the inner wall of the mold and the slab.

15 12. The continuous casting method of a Cu alloy according to any one of claims 6 to 11, wherein the Cu alloy contains, by mass %, one or more components selected from Cr: 0.01 to 5%, Ti: 0.01 to 5%, Zr: 0.01 to 5%, Nb: 0.01 to 5%, Ta: 0.01 to 5%, Al: 0.01 to 5%, Mo: 0.01 to 5%, V: 0.01 to 5%, Co: 0.01 to 5%, Mn: 0.01 to 5%, Si: 0.01 to 5%, Be: 0.01 to 5%, and Hf: 0.01 to 5%.

20 13. The continuous casting method of a Cu alloy according to claim 12, wherein the Cu alloy further contains, by mass %, 0.001 to 5 % in total of one or more of the alloy components selected from at least one group of the following three groups:

25 First group: 0.001 to 1 mass% in total of one or more selected from P, B, Sb, Bi, Pb, Cd, S and As;
Second group: 0.01 to 5 mass% in total of one or more selected from Sn, Ag, Zn, Ni, Au, Pd, Fe, W, In and Ge; and
Third group: 0.01 to 3 mass% in total of one or more selected from Te, Se, Sr, T1, Rb, Cs, Ba, Re, Os, Rh, Po, Ga, Tc, Ru, Pd, Ir, Pt and Ta.

25 14. The continuous casting method of a Cu alloy according to claim 12 or 13, wherein the Cu alloy further contains, by mass %, 0.001 to 2% in total of one or more of alloy components selected from Li, Ca, Mg and rare earth elements.

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Fig.1

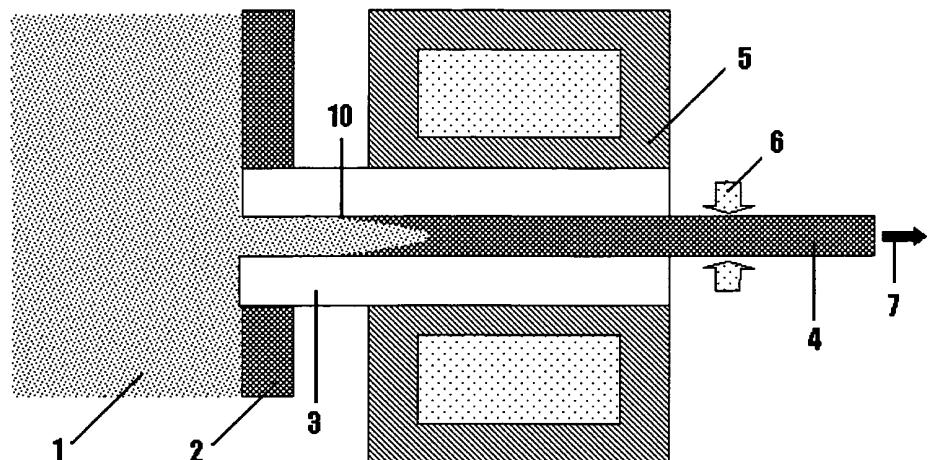


Fig.2

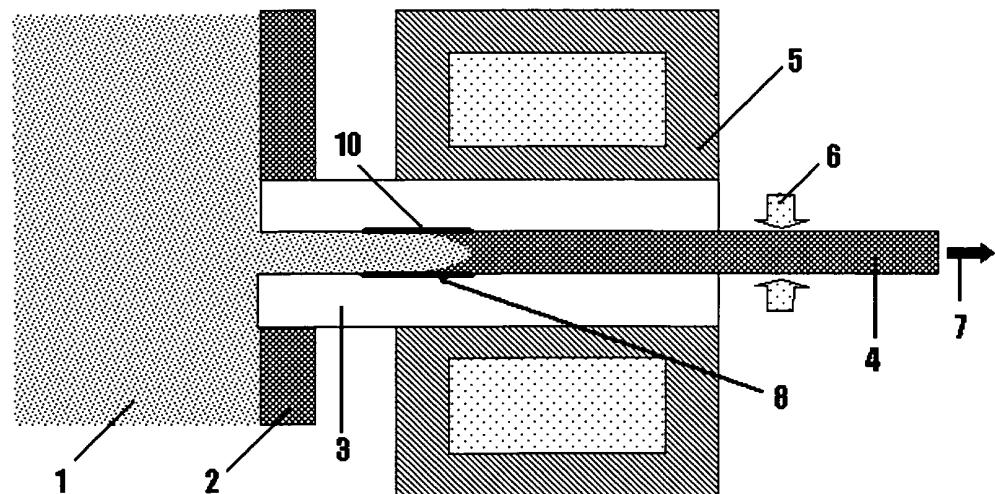


Fig.3

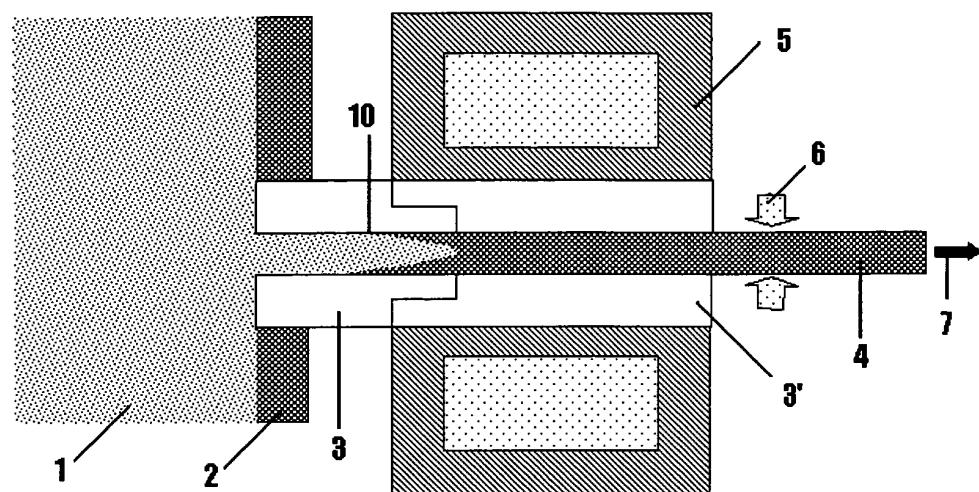


Fig.4

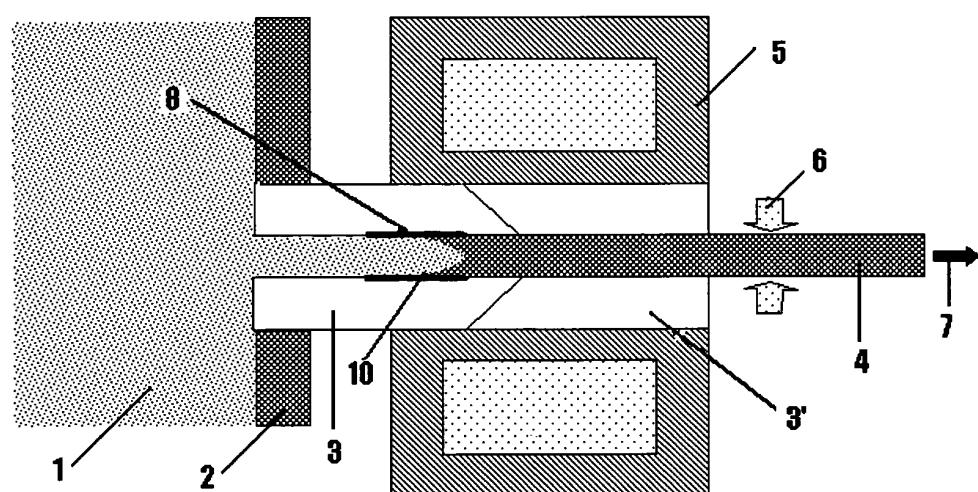


Fig.5

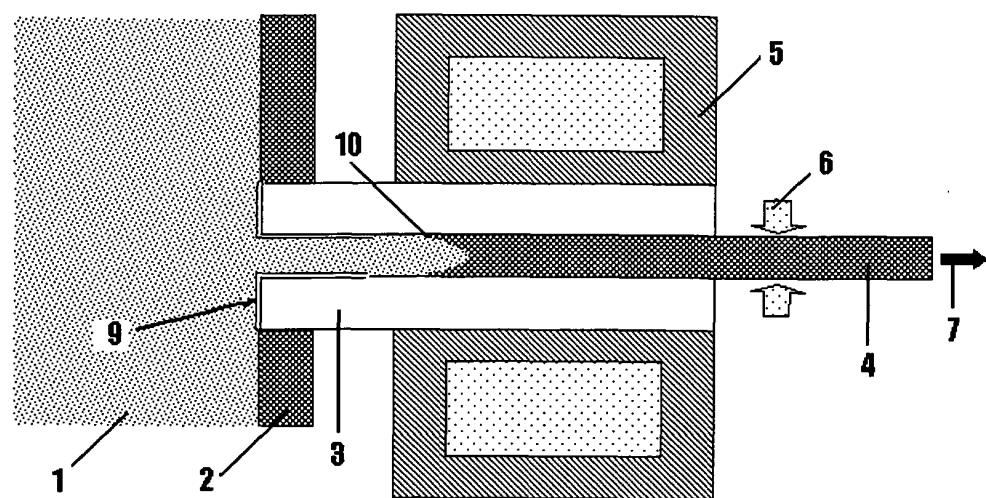


Fig.6

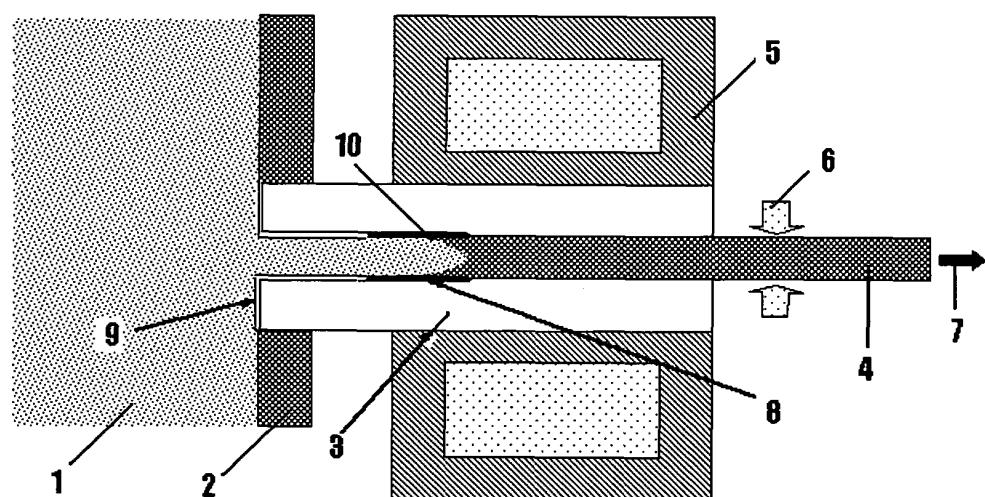


Fig.7

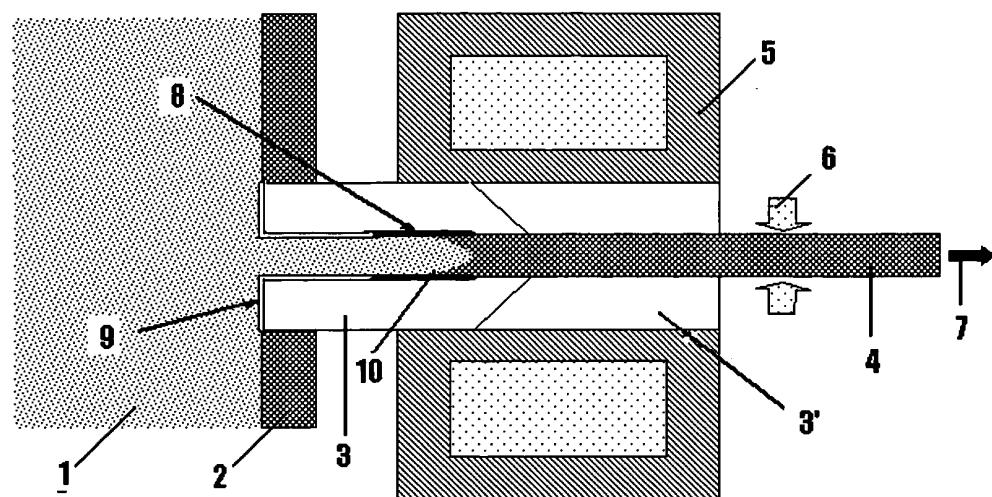


Fig.8

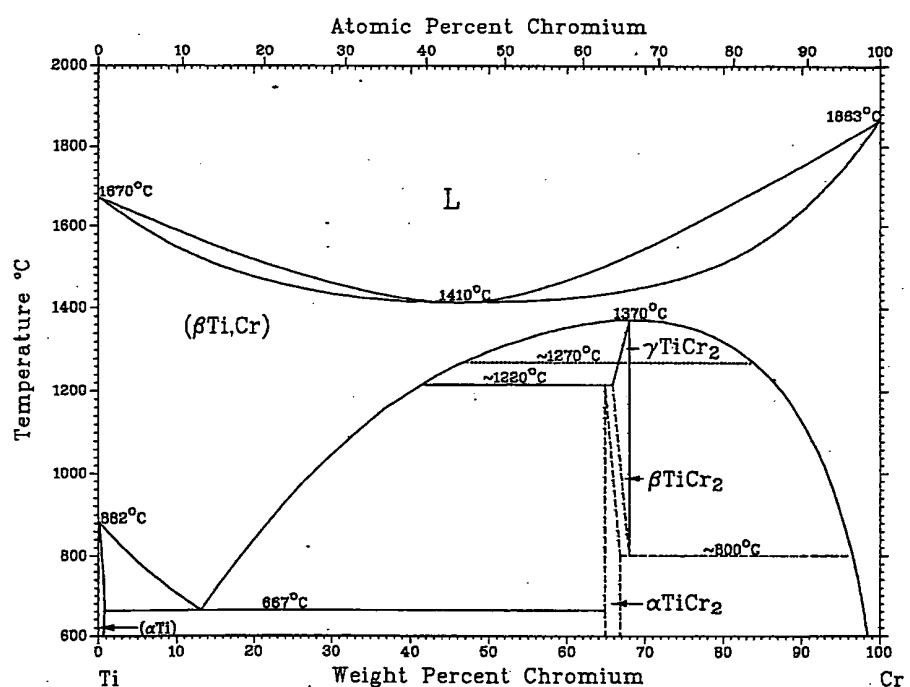


Fig.9

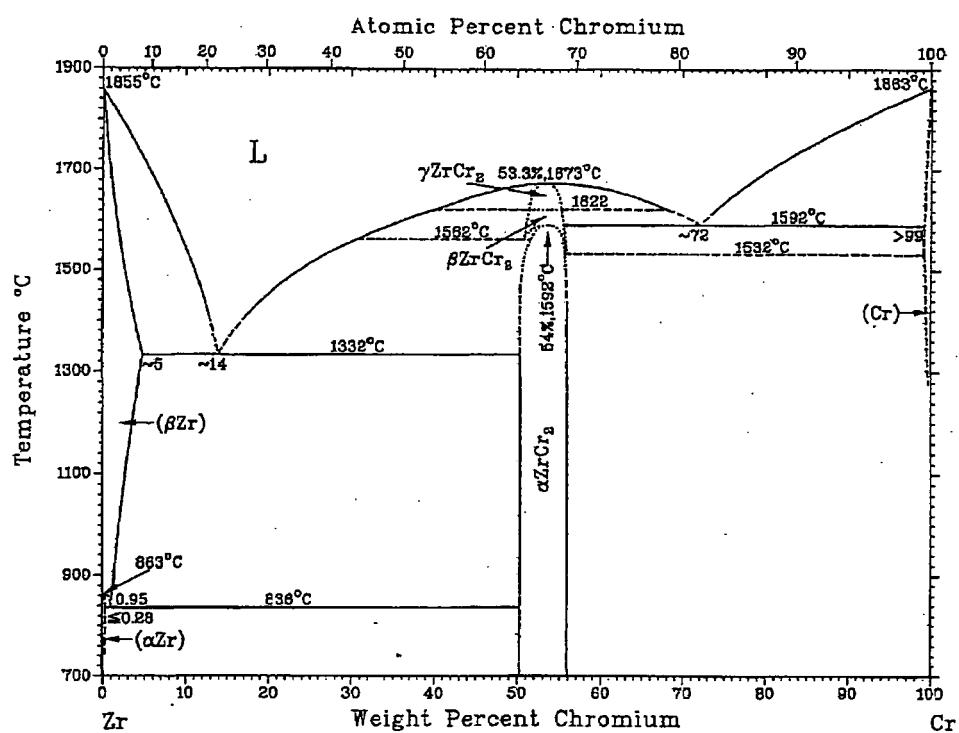
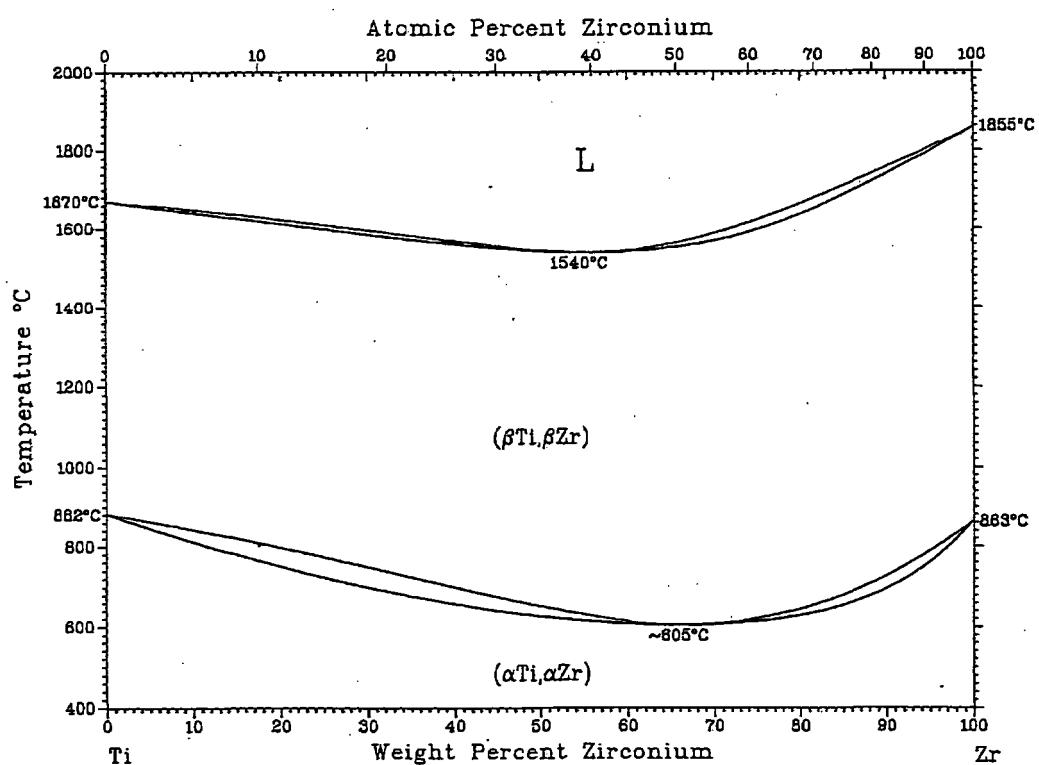


Fig.10



INTERNATIONAL SEARCH REPORT		International application No. PCT/JP2004/013756
A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ B22D11/00, B22D11/059, B22D11/053, B22D11/07, B22D21/00, B22D11/04, C22C9/00, C22C9/10, C22C9/05		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ B22D11/00, B22D11/059, B22D11/053, B22D11/07, B22D21/00, B22D11/04, C22C9/00, C22C9/10, C22C9/05		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 5-318034 A (The Furukawa Electric Co., Ltd.), 03 December, 1993 (03.12.93), Claim 1; Par. Nos. [0010] to [0011]; Fig. 2 (Family: none)	1,2,5,6, 10-14
Y	JP 9-141394 A (Sumitomo Metal Industries, Ltd.), 03 June, 1997 (03.06.97), Claims 1 to 3; Fig. 1; Par. Nos. [0014] to [0032] (Family: none)	1,2,5,6, 10-14
X	JP 11-147162 A (Tokai Carbon Co., Ltd.), 02 June, 1999 (02.06.99), Claim 1; Par. Nos. [0011] to [0019] (Family: none)	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 15 December, 2004 (15.12.04)		Date of mailing of the international search report 28 December, 2004 (28.12.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer Telephone No.
Facsimile No.		

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/013756

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 6-179930 A (Tatsuta Electric Wire & Cable Co., Ltd.), 28 June, 1994 (28.06.94), Claims 1 to 3; Par. Nos. [0009] to [0012]; Fig. 2 (Family: none)	5, 6, 10-14
Y	JP 61-169149 A (Japan Energy Corp.), 30 July, 1986 (30.07.86), Claim 1; page 2, upper right column, line 4 to page 3, upper left column, line 13; Fig. 4 (Family: none)	6-14
Y	JP 3-210942 A (Sumitomo Metal Industries, Ltd.), 13 September, 1991 (13.09.91), Claims; page 2, lower left column, line 12 to lower right column, line 12; Fig. 1 (Family: none)	7, 9-11
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