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(54) **TITANIUM COPPER PLATE, PRESSED PRODUCT, AND PRESSED-PRODUCT
MANUFACTURING METHOD**

(57) Provided is a titanium copper plate having improved strength stability and discoloration resistance after a heat treatment. The titanium copper plate contains from 2.0 to 4.5% by mass of Ti, the balance being copper and inevitable impurities, wherein a peak aging temperature at which a maximum value (TS_{max}) of a tensile strength in a direction parallel to a rolling surface and perpendicular to a rolling direction is obtained is 420 °C or less, and the TS_{max} is from 800 to 1200 MPa, wherein

a ratio (TS_1 / TS_{max}) of a tensile strength TS_1 in the perpendicular direction after a heat treatment at a temperature which is higher by 20 °C than the peak aging temperature to the TS_{max} is 0.98 or more, and wherein a ratio (TS_2 / TS_{max}) of a tensile strength TS_2 in the perpendicular direction after the heat treatment at a temperature which is lower by 20 °C than the peak aging temperature for 2 hours to the TS_{max} is 0.98 or more.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a titanium copper plate, a pressed product, and a method for manufacturing a pressed product. More particularly, it relates to a titanium copper plate which is a non-mill hardened material that is subjected to a heat treatment after pressing, and which can be suitably used as a member for electronic parts such as connectors, a pressed product and a method for manufacturing the pressed product.

BACKGROUND OF THE INVENTION

[0002] Recently, miniaturization of electronic devices represented by portable terminals is increasingly progressing, and connectors used in the electronic devices are bringing about remarkable tendencies to narrow the pitch and reduce the height. A smaller connector has a narrower pin width, resulting in a smaller folded shape, so that the member to be used is required to have both high strength in order to obtain required springiness and excellent bendability that can withstand severe bending. In this respect, a copper alloy containing titanium (hereinafter referred to as "titanium copper") has a relatively high strength and the best stress relaxation property among copper alloys. Therefore, the demand of the titanium copper has been increased as a terminal member for signal systems.

[0003] Titanium copper is generally known to be an age hardening type copper alloy. Specifically, when a supersaturated solid solution of Ti which is a solute atom is formed by a solutionizing treatment, and in this state, a heat treatment is carried out at a low temperature for a relatively long period of time, a modulated structure which is a periodical variation in the Ti concentration is developed in a matrix due to spinodal decomposition, so that the intensity is increased. Based on such a strengthening mechanism, various techniques are being studied with the aim of further improvement of characteristics of titanium copper. In this case, the problem is that the strength and the bendability are contradictory characteristics. That is, if the strength is improved, the bendability is impaired, while if the bendability is emphasized, the desired strength cannot be obtained. Therefore, the research and development have been made in order to achieve both the strength and the bendability of titanium copper, from the viewpoints such as addition of a third element such as Fe, Co, Ni, and Si (Patent Literature 1); control of the concentration of impurity element groups that are subjected to solid solution in a matrix and precipitation of these in a certain distribution form as second phase grains (Cu-Ti-X-based grains) to increase ordered properties of the modulated structure (Patent Literature 2); and defining of densities of a trace amount of elements and second phase grains effective to refine crystal grains (Patent Literature 3).

[0004] It is generally known that if the second phase grains become too coarse in the process of manufacturing titanium copper, the bendability tends to be impaired. Therefore, in the conventional final solutionizing treatment, the material is heated to a predetermined temperature, and then cooled at a cooling rate as fast as possible by means of water cooling or the like to suppress the precipitation of the second phase grains in the cooling process. For example, Japanese Patent Application Publication No. 2001-303222 A (Patent Literature 4) discloses an example of rapidly cooling a material at a cooling rate of 200 K (200 °C)/sec or more after the heat treatment of the material in order to suppress variations in characteristics. Further, Japanese Patent Application Publication No. 2002-356726 A (Patent Literature 5) discloses a titanium-copper alloy resulting in a desired bending radius ratio when conducting a W bending test in a direction perpendicular to a rolling direction, in order to increase the strength without impairing the bendability.

CITATION LIST

Patent Literatures

[0005]

[Patent Literature 1] Japanese Patent Application Publication No. 2004-2319857 A

[Patent Literature 2] Japanese Patent Application Publication No. 2004-176163 A

[Patent Literature 3] Japanese Patent Application Publication No. 2005-97638 A

[Patent Literature 4] Japanese Patent Application Publication No. 2001-303222 A

[Patent Literature 5] Japanese Patent Application Publication No. 2002-356726 A

SUMMARY OF THE INVENTION

Technical Problem

[0006] When manufacturing electronic parts such as connectors by pressing, there is a problem that materials having

higher strength cause significant spring-back after bending and dimensions after pressing are beyond target dimensions. There is also a problem that a spring limit value is lowered due to the introduction of strain by pressing. Therefore, a type of material (hereinafter, referred to as a non-mill hardened material) would be considered which has improved strength and spring limit value by pressing a material having relatively low strength, which has been subjected to finish cold rolling after solid solution, to obtain desired dimensions, and then performing a heat treatment. As an alloy having high strength and conductivity by performing the heat treatment after pressing, a material in which Be is added to Cu is known in the art, and for example, C 17200 (1.8 to 2.0% by mass of Be, 0.2% by mass or more of Ni + Co, the balance being Cu) has been registered in CDA (Copper Development Association). Further, in titanium copper, there is a non-mill hardened material that is subjected to a heat treatment after pressing.

[0007] When the non-mill hardened titanium copper is subjected to a heat treatment after pressing, the pressed product is placed in a furnace set to a predetermined temperature in a nitrogen or argon gas atmosphere, maintained for several hours, and then taken out. In this case, the material temperature varies depending on a position of the pressed product placed in the furnace, and whether it is on an outer peripheral side or on an inner side of a reel if it is wound in a reel shape, resulting in a problem that the strength varies between lots and within lots. In particular, Patent Literature 5 mentions titanium copper in which a heat treatment is carried out after pressing and a hardness after the heat treatment is 345 Hv or more. However, when the material temperature is shifted from a recommended heat treatment temperature, the strength is sharply changed.

[0008] There is also a problem that a trace amount of water vapor, oxygen or nitrogen in the atmospheric gas reacts with titanium in the titanium copper, thereby causing discoloration on the surface due to the heat treatment. Titanium oxides and titanium nitrides that cause discoloration require chemical polishing due to deterioration of plating adhesion and appearance problems even if plating is not performed.

[0009] In addition, the titanium copper (mill hardened material) that has undergone the heat treatment before pressing is placed in a heat treatment furnace with a strip material wound in a coil shape, and heated, soaked, and cooled. Therefore, aged precipitation is promoted under all conditions of heating from an ambient temperature, soaking at a target temperature and cooling to the ambient temperature (slow cooling). As a result, a peak aging temperature at which the maximum tensile strength is obtained is found at a temperature of 420 °C or less. On the other hand, non-mill hardened titanium copper is charged (rapidly heated) into a furnace conditioned at a predetermined temperature, maintained, and taken out (air-cooled), so that precipitation occurs only during the maintaining. Therefore, the precipitation tends to be insufficient as compared with the mill hardened material. For the above reasons, the peak aging temperature of the non-mill hardened material tends to exceed 420 °C, and the temperature range results in easy discoloration.

[0010] Therefore, an object of the present invention is to provide a titanium copper plate which is a non-mill hardened material of titanium copper which is subjected to a heat treatment after pressing, and which has a decreased variation in strength between lots after a heat treatment and less discoloration after the heat treatment.

Solution to Problem

[0011] As a results of intensive studies for a variation in strength between lots in a direction parallel to a rolling surface and perpendicular to a rolling direction (hereinafter, referred to as a "rolling perpendicular direction) after subjecting a titanium copper plate to a heat treatment at a peak aging temperature, and a discoloration property after the heat treatment, in order to solve the above problems, the present inventors have found that a tensile strength after the heat treatment at a temperature which is different by 20 °C from the peak aging temperature is comparable to the tensile strength in the rolling perpendicular direction after the heat treatment at the peak aging temperature, which is advantageous for improving strength stability between lots, and that discoloration is suppressed by decreasing the peak aging temperature to 420 °C or less. Furthermore, they have found that the titanium copper plate can be obtained by solutionizing treatment conditions as described later, a material temperature at the initiation of hot rolling, and a rolling workability, and have arrived at the present invention.

[0012] Thus, in an aspect, the present invention relates to a titanium copper plate, the titanium copper plate containing from 2.0 to 4.5% by mass of Ti, the balance being copper and inevitable impurities, wherein a peak aging temperature at which a maximum value (TS_{max}) of a tensile strength in a direction parallel to a rolling surface and perpendicular to a rolling direction is obtained is 420 °C or less, and the TS_{max} is from 800 to 1200 MPa, wherein a ratio (TS_1 / TS_{max}) of a tensile strength TS_1 in the perpendicular direction after a heat treatment at a temperature which is higher by 20 °C than the peak aging temperature to the TS_{max} is 0.98 or more, and wherein a ratio (TS_2 / TS_{max}) of a tensile strength TS_2 in the perpendicular direction after the heat treatment at a temperature which is lower by 20 °C than the peak aging temperature for 2 hours to the TS_{max} is 0.98 or more.

[0013] In one embodiment of the titanium copper plate according to the present invention, the ratio: TS_1 / TS_{max} is 0.99 or more, and the ratio: TS_2 / TS_{max} is 0.99 or more.

[0014] In one embodiment of the titanium copper plate according to the present invention, the TS_{max} is from 800 to 1100 MPa.

[0015] In one embodiment of the titanium copper plate according to the present invention, the titanium copper plate has a conductivity of from 8 to 20% IACS after the heat treatment at the peak aging temperature for 2 hours.

[0016] In one embodiment of the titanium copper plate according to the present invention, further comprising at least one third element selected from the group consisting of Fe, Co, Mg, Si, Ni, Cr, Zr, Mo, V, Nb, Mn, B, and P in a total amount of 0.5% by mass or less.

[0017] Further, in another aspect, the present invention relates to a pressed product comprising the titanium copper plate.

[0018] Further, another aspect of the present invention relates to a method for manufacturing a pressed product, comprising subjecting any one of the above titanium copper plates to pressing and an aging treatment in this order.

Advantageous Effects of Invention

[0019] According to the present invention, it is possible to obtain a titanium copper plate having improved strength stability and discoloration resistance after a heat treatment. Since the titanium copper plate according to the present invention has improved strength stability after the heat treatment, it can be suitably used for the production of small electronic components manufactured by carrying out a heat treatment after pressing, which have a decreased variation in strength between lots.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention will be described below in detail with reference to preferred embodiments. It should be understood that the present invention is not limited to the following embodiments, and various modifications may be made without changing the spirit of the present invention.

[1. Titanium Copper Plate]

[0021] In an embodiment, the present invention provides a titanium copper plate, the titanium copper plate containing from 2.0 to 4.5% by mass of Ti, the balance being copper and inevitable impurities, when a heat treatment is carried out at 300 to 500 °C for 2 hours, wherein a peak aging temperature at which a maximum value (TS_{max}) of a tensile strength in a direction parallel to a rolling surface and perpendicular to a rolling direction is obtained is 420 °C or less, and the TS_{max} is from 800 to 1200 MPa, and wherein a ratio (TS_1 / TS_{max}) of a tensile strength TS_1 in the perpendicular direction after a heat treatment at a temperature which is higher by 20 °C than the peak aging temperature to the TS_{max} is 0.98 or more, and wherein a ratio (TS_2 / TS_{max}) of a tensile strength TS_2 in the perpendicular direction after the heat treatment at a temperature which is lower by 20 °C than the peak aging temperature for 2 hours to the TS_{max} is 0.98 or more. Hereinafter, preferable embodiments of each component will be described.

(Ti Content)

[0022] In an embodiment of the titanium copper plate according to the present invention, the Ti content is from 2.0 to 4.5% by mass in order to increase the strength by leading to solid solution of Ti in the Cu matrix by a solutionizing treatment, and dispersing fine precipitates in the alloy by an aging treatment. The lower limit of the Ti content is 2.0% by mass or more, and preferably 2.5% by mass or more, and more preferably 2.7% by mass or more, in terms of obtaining sufficient strength after the heat treatment. Further, the upper limit of the Ti content is 4.5% by mass or less, and preferably 4.0% by mass or less, and more preferably 3.5% by mass or less, in terms of suppressing fracture of a material in hot rolling and having improved bendability.

(Third Element)

[0023] The titanium copper plate according to the present invention can optionally contain a predetermined third element in addition to copper and titanium, and the third element-containing titanium copper plate can be used. In a preferred embodiment, the titanium copper plate may contain at least one selected from the group consisting of Fe, Co, Mg, Si, Ni, Cr, Zr, Mo, V, Nb, Mn, B, and P as the third element, in a total amount of 0.5% by mass or less. However, the total content of these elements may be zero, that is, these elements may not be contained. For example, the titanium copper plate can contain them in the range of from 0.01 to 0.5% by mass, and preferably from 0.01 to 0.3% by mass, and more preferably from 0.05 to 0.3% by mass, and it can be used. Although the age hardening of titanium copper can be improved by adding such a third element, titanium copper to which no third element is added would also exert the advantageous effects of the present invention.

[0024] Further, an amount of Fe added is preferably 0.5% by mass or less, and more preferably 0.25% by mass or

less. An amount of Co added is preferably 0.5% by mass or less, and more preferably 0.1% by mass or less. An amount of Mg added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Si added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Ni added is preferably 0.5% by mass or less, and more preferably 0.1% by mass or less. An amount of Cr added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Zr added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Mo added is preferably 0.5% by mass or less, and more preferably 0.3% by mass or less. An amount of V added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Nb added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of Mn added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of B added is preferably 0.1% by mass or less, and more preferably 0.05% by mass or less. An amount of P added is preferably 0.5% by mass or less, and more preferably 0.1% by mass or less. However, the amounts added are not limited to the above amounts.

(Thickness)

[0025] The product has a thickness, i.e., a thickness (t), of preferably from 0.02 to 1.5 mm. The thickness is not particularly limited, but if the thickness is too high, bending will become difficult.

(Peak Aging Temperature)

[0026] In the present invention, the peak aging temperature can be confirmed by determining the maximum value (TS_{max}) of the tensile strength in the rolling perpendicular direction when the heat treatment is carried out at 300 to 500 °C for 2 hours. For example, eleven titanium copper plates are prepared as specimens, and adjusted to a temperature of 300 to 500 °C in units of 20 °C, and the specimens corresponding to each temperature condition are subjected to the heat treatment in an argon atmosphere for 2 hours. The tensile strength in the rolling perpendicular direction is then measured for each specimen. The maximum value TS_{max} of the tensile strength for each specimen is determined, and the peak aging temperature at the time of this TS_{max} is confirmed. In this case, from the viewpoint of having strength stability and discoloration resistance, the peak aging temperature at which the above TS_{max} was obtained is preferably 420 °C or less.

[0027] It should be noted that the tensile strength is measured using a tensile tester in accordance with JIS Z 2241 (2011).

(Tensile Strength)

[0028] The TS_{max} of the tensile strength in the rolling perpendicular direction is preferably from 800 to 1200 MPa. In view of the use as a spring material, the lower limit of TS_{max} is preferably 800 MPa or more, and more preferably 850 MPa or more, and further preferably 900 MPa or more. On the other hand, the upper limit of the TS_{max} is preferably 1200 MPa or less, and more preferably 1150 MPa or less, and further preferably 1100 MPa or less, in terms of good strength stability during the heat treatment. The reason for focusing on the rolling perpendicular direction is that a property which will affect the springiness of a general connector is the strength in the rolling perpendicular direction.

[0029] Further, when the heat treatment is carried out at a temperature which is higher by 20 °C than the peak aging temperature for 2 hours, the tensile strength TS_1 in the rolling perpendicular direction is measured, and when the heat treatment is further carried out at a temperature which is lower by 20 °C than the peak aging temperature for 2 hours, the tensile strength TS_2 in the rolling perpendicular direction is measured. From the viewpoint of improving the strength stability after the heat treatment, the ratios TS_1 / TS_{max} and TS_2 / TS_{max} are preferably 0.98 or more, respectively, and more preferably 0.985 or more, respectively, and even more preferably 0.99 or more, respectively. Each of the ratios TS_1 / TS_{max} and TS_2 / TS_{max} is at most 1.00.

(Conductivity)

[0030] The conductivity of the titanium copper plate after the heat treatment at the peak aging temperature for 2 hours is preferably from 8 to 20% IACS. The lower limit of the conductivity is preferably 8% IACS or more, and more preferably 9% IACS or more, and further preferably 10% IACS, from the viewpoint that the titanium copper plate is satisfactorily used for electronic component applications. Further, the upper limit of the conductivity is preferably 20% IACS or less, and more preferably 18% IACS or less, and further preferably 16% IACS or less, from the viewpoint of ensuring strength stability after the heat treatment.

[0031] It should be noted that the conductivity is measured in accordance with JIS H 0505.

(Strength Stability)

[0032] According to a strength stability test, a variation in strength between lots after the heat treatment can be confirmed. For example, a plurality of titanium copper plates are collected for predetermined sizes, the resulting samples are stacked and fixed with copper number wires, and the heat treatment is carried out at the peak aging temperature for 2 hours. For those samples, the tensile strength in the rolling perpendicular direction is investigated to determine the maximum, minimum, and average values of the obtained tensile strength. Subsequently, A and B are calculated: $A (\%) = \{(\text{maximum value} - \text{average value}) / \text{average value}\} \times 100$; and $B (\%) = \{(\text{average value} - \text{minimum value}) / \text{average value}\} \times 100$. In this case, each of the A and B is preferably 10% or less, and more preferably 5% or less, in terms of reducing a change in strength at the peak aging temperature.

[0033] The tensile strength is measured using a tensile tester in accordance with JIS Z 2241 (2011).

(Discoloration Resistance)

[0034] According to the discoloration resistance in the present invention, it can be confirmed that the titanium copper plate has less discoloration after the heat treatment. For example, a solder wettability after pickling with dilute sulfuric acid is evaluated after the heat treatment for 2 hours at the peak aging temperature in an atmosphere of an argon gas having a purity of 99.9 vol% or more. A solder wettability measuring device is used, and a mixed solution of 25 vol% of rosin and 75 vol% of ethanol is used as a flux. A specimen is obtained by cutting a titanium copper plate into a width of 10 mm and a length of 30 mm such that the rolling perpendicular direction is the longitudinal direction, and the specimen is then immersed in 10 vol% of dilute sulfuric acid for 10 seconds as a pretreatment, and washed with water and dried. As the solder bath, a molten solder bath in which Sn-3% by mass Ag-0.5% by mass Cu is dissolved and maintained at 245 °C is used. One end of the specimen in the longitudinal direction is immersed in the solder bath under conditions of an immersion rate of 5 mm/s, an immersion depth of 12 mm, and an immersion time of 10 seconds, and a wetting height after the solder wetting test is measured. In this case, the wetting height is preferably 6 mm or more, and more preferably 12 mm or more, in terms of preventing discoloration after the titanium copper plate is subjected to the heat treatment. When the titanium copper plate has a little discoloration after the heat treatment, it can be used as a product without pickling and polishing after the heat treatment. For example, the pretreatment such as chemical polishing can be omitted even if plating is carried out.

[2. Method for Manufacturing Titanium Copper Plate]

[0035] In a general manufacturing process of the titanium copper plate, first, raw materials such as electrolytic copper and Ti are melted in a melting furnace to obtain a molten metal having a desired composition. The molten metal is then cast into an ingot. In order to prevent oxidative wear and tear of titanium, the melting and casting are preferably carried out in vacuum or in an inert gas atmosphere. After that, hot rolling, cold rolling, and a solutionizing treatment are carried out in this order to finish a plate having a desired thickness and characteristics. After the solutionizing treatment, the surface may be washed with an acid or polished in order to remove surface oxide films formed during the heat treatment. Further, in order to increase the strength, cold rolling may be carried out after the solutionizing treatment. The desired properties and shape are then obtained by pressing and a heat treatment by a press maker.

[0036] The titanium copper plate according to the present invention can be manufactured by carrying out, in particular, the solutionizing treatment and a finish rolling step immediately after the solutionizing treatment, under appropriate conditions. Hereinafter, suitable production examples will be sequentially described for each step.

1) Production of Ingot

[0037] Production of the ingot by melting and casting is basically carried out in a vacuum or in an inert gas atmosphere. If the additive element remains non-melted during melting, it does not effectively act on improvement of strength. Therefore, in order to eliminate non-melted residue, a high melting point third element such as Fe and Cr should be sufficiently agitated after being added, and then maintained for a certain period of time. On the other hand, since Ti is relatively easily dissolved in Cu, it may be added after the third element is melted. Therefore, it is desirable that to Cu is added at least one selected from the group consisting of Fe, Co, Mg, Si, Ni, Cr, Zr, Mo, V, Nb, Mn, B, and P as the third element so as to contain them in a total amount of 0.5% by mass or less, and Ti is then added as a second element so as to contain it in an amount of from 2.0 to 4.5% by mass to produce the ingot. However, the amount of the third element added is preferably 0.05% by mass or more. It should be noted that the order of adding Ti and the third element to Cu is not particularly limited.

2) Homogenized Annealing and Hot Rolling

[0038] Since solidifying segregation and crystallized matters produced during the production of the ingot are coarse, it is desirable to dissolving them in the matrix phase as much as possible to decrease them, and eliminate them as much as possible, by homogenized annealing. This is because it is effective in preventing cracks due to bending. More particularly, after the ingot production step, homogenized annealing is preferably carried out by heating the material at 900 to 970 °C for 3 to 24 hours, and the hot rolling is then preferably carried out. In order to prevent liquid metal embrittlement, it is preferable that a temperature before and during the hot rolling is preferably 960 °C or less.

3) Solutionizing Treatment

[0039] It is preferable that the solutionizing treatment is then carried out after repeating the cold rolling and annealing as needed. In the present invention, a temperature of the solutionizing is preferably from 750 °C to 900 °C. The lower limit of the solutionizing temperature is preferably 750 °C or more, and more preferably 775 °C or more, and even more preferably 790 °C or more, from the viewpoints that recrystallization is sufficient, the ratios TS_1 / TS_{max} and TS_2 / TS_{max} after the heat treatment are higher, and the strength stability after the heat treatment is improved at the peak aging temperature. On the other hand, the upper limit of the solutionizing temperature is preferably 900 °C or less, and more preferably 875 °C or less, and still more preferably 850 °C or less, from the viewpoint that the TS_{max} after the heat treatment is 800 MPa or more. A temperature rising rate at this time is preferably as fast as possible.

[0040] On the other hand, it is important to adjust a cooling rate during the solutionizing treatment to generate precipitation nuclei at the cooling after the solutionizing. A cooling rate is preferably 50 to 300 °C/sec. The lower limit of the cooling rate is preferably 50 °C/sec or more, and more preferably 75 °C/sec or more, and even more preferably 100 °C/sec or more, from the viewpoints that precipitation is suppressed to have moderate nucleation, the conductivity after peak aging is 20% IACS or less, and the above TS_1 / TS_{max} and TS_2 / TS_{max} after the heat treatment are in the desired range and the strength stability after the heat treatment at the peak aging temperature. Further, the upper limit of the cooling rate is preferably 300 °C/sec or less, and more preferably 275 °C/sec or less, and further preferably 250 °C/sec or less, from the viewpoints that the formation of precipitated nuclei takes place without excess or deficiency, the peak aging temperature is 420 °C or less, and the discoloration after the heat treatment is prevented. As used herein, an average cooling rate refers to a value (°C/sec) determined by measuring a time required for cooling from a cooling initiation time, for example, 750 °C, from 100 °C (cooling time), and calculating the value by the equation: $(750 - 100) (°C) / \text{cooling time (seconds)}$.

4) Finish Rolling

[0041] After the solutionizing treatment, hot finish rolling (hereinafter, also referred to as "hot rolling") is carried out. In a preferred embodiment, the workability (rolling ratio) of the hot rolling is preferably from 10 to 70%. The lower limit of the rolling ratio is preferably 10% or more, and more preferably 20% or more, and still more preferably 25% or more, from the viewpoint that TS_{max} is 800 MPa or more. However, the upper limit of the rolling ratio is preferably 70% or less, and more preferably 60% or less, and still more preferably 50% or less, from the viewpoints that the TS_{max} is adjusted to be 1200 MPa or less and the ratios TS_1 / TS_{max} and TS_2 / TS_{max} after the heat treatment are maintained in the suitable range, thereby improving the strength stability during the heat treatment. The rolling ratio R is defined by the equation: $R (\%) = ((\text{thickness before rolling} - \text{thickness after rolling}) / \text{thickness before rolling}) \times 100$.

[0042] Further, a temperature of the material at the end of the hot rolling (hereinafter referred to as a hot rolling temperature) is preferably adjusted to a range of from 360 to 460 °C. When the hot rolling is carried out in the above range, the precipitates generated in the cooling process after the solutionizing grow by the hot rolling and new precipitates are precipitated, so that the peak aging temperature after pressing is decreased, and the ratio TS_{min} / TS_{max} is in the desired range, thereby improving the strength stability during the heat treatment. For example, the hot rolling temperature is preferably from 360 to 420 °C. The lower limit of the hot rolling temperature is preferably 360 °C or more, and more preferably 380 °C or more, and even more preferably 390 °C or more, from the viewpoints that the peak aging temperature is 420 °C or less and the conductivity after peak aging is 8% IACS or more because the precipitated nuclei are sufficiently dispersed. On the other hand, the upper limit of the hot rolling temperature is preferably 460 °C or less, and more preferably 450 °C or less, and still more preferably 440 °C or less, from the viewpoints that the ratios TS_1 / TS_{max} and TS_2 / TS_{max} after the heat treatment are in the desired range without coarsening the precipitates, and the strength stability during the heat treatment is improved. However, when only cold rolling is carried out without performing the hot rolling, the peak aging temperature more than 420 °C deteriorates the discoloration resistance, and also decreases the above ratios TS_1 / TS_{max} and TS_2 / TS_{max} after the heat treatment, so that the strength stability during the heat treatment tends to be deteriorated. Since it is difficult to determine a degree of dispersion of fine precipitates and a degree of dispersion of coarse precipitates from the conductivity after the hot rolling, it is important to control the above temperature.

[0043] A person skilled in the art would understand that grinding, polishing, shot blast pickling, degreasing, and the like for removing oxide scales on the surface can be optionally carried out between the above steps and after the finish rolling.

[3. Method for Manufacturing Pressed Product]

[0044] The titanium copper plate manufactured by the manufacturing method as described above is subjected to pressing and an aging treatment by a press maker to have desired characteristics and shape. For example, the pressing and the aging treatment are carried out in this order. The pressing and the aging treatment are carried out under typical conditions. A temperature of the aging treatment may preferably be from 360 to 420 °C so as to have improved strength stability and discoloration resistance of the material after the treatment. Further, a time of the aging treatment may preferably be from 0.5 to 4 hours. The pressed product includes the titanium copper plate manufactured by the above manufacturing method.

EXAMPLES

[0045] Hereinafter, while Examples of the present invention are shown below together with Comparative Examples, these are provided for better understanding of the present invention and its advantages, and are not intended to limit the invention.

[Production of Titanium Copper]

[0046] When the titanium copper plates of each Example and each Comparative Example were produced, Ti which was an active metal was added as a second element. Therefore, the melting practice employed a vacuum melting furnace. Further, relatively high-purity raw materials were carefully selected and used in order to prevent unexpected side effects due to contamination with impurity elements other than those specified in the present invention.

[0047] The Ti having each Ti concentration was added, and optionally each third element as shown in Table 1 was further added to obtain an ingot having a composition in which the balance was copper and inevitable impurities. The ingot was subjected to homogenized annealing by heating it at 950 °C for 3 hours, followed by hot rolling at 900 to 950 °C, to provide a hot-rolled plate having a thickness of 10 mm. After descaling by face cutting, the cold rolling was carried out. The solutionizing treatment and water cooling were then carried out under the conditions as shown in Table 1. More specifically, a specimen was placed in an electric furnace, and removed at the time when the material temperature as shown in Table was reached, and placed in a water tank or a furnace that was maintained at a predetermined temperature to cool the specimen, while measuring the material temperature with a thermocouple. It should be noted that the material temperature was measured with the thermocouple installed in the electric furnace. The cooling rate (°C/sec) except for the water cooling was determined from the cooling time from the solutionizing temperature to the final temperature of 100 °C for the material temperature measured with the thermocouple.

[0048] Subsequently, after descaling by washing with an acid, and when initiating the rolling as final rolling, the hot rolling (a thickness of 0.15 mm) was then carried out while adjusting the material temperature to that shown in Table 1 and adjusting the rolling ratio to that shown in Table 1.

[0049] Each specimen prepared as described above was characterized under the following conditions:

[Component]

[0050] The alloy element concentration of each specimen was analyzed by ICP-mass spectrometry. As a result, it was substantially the same as the composition ratio of the added elements.

[Peak Aging Temperature Test and Tensile Strength]

[0051] Eleven specimens were prepared for each test number. These specimens were subjected to a heat treatment at 300 °C to 500 °C in units of 20 °C, and a relationship between the heat treatment temperature and the tensile strength of the specimen was investigated. More specifically, a first specimen was placed in a furnace heated to a furnace temperature of 300 °C in an argon gas atmosphere having a purity of 99.9 vol%, heated for 2 hours, and then taken out and cooled to room temperature. For each specimen after the heat treatment, the tensile strength in the rolling perpendicular direction was measured using a tensile tester according to JIS Z 2241 (2011) such that the longitudinal direction of each specimen was the rolling perpendicular direction. A second specimen was subjected to the same heat treatment as that for the first specimen with the exception that the furnace temperature was changed to 320 °C, and the tensile strength in the rolling perpendicular direction was measured. Similarly, by changing the heat treatment temperatures by

20 °C, the tensile strength in the rolling perpendicular direction was measured for all 11 specimens. Thus, the peak aging temperature and the tensile strength $TS_{\max}$ at this temperature were investigated. Further, the tensile strength TS_1 of each specimen subjected to the aging treatment at a temperature which was higher by 20 °C than the peak aging temperature, and the tensile strength TS_2 of each specimen subjected to the aging treatment at a temperature which was lower by 20 °C than the peak aging temperature were confirmed. Then, the ratios $TS_1 / TS_{\max}$ and $TS_2 / TS_{\max}$ were calculated. It should be noted that table 2 shows a lower value of the values of $TS_1 / TS_{\max}$ and $TS_2 / TS_{\max}$.

[Conductivity]

[0052] The specimens were charged at each peak aging temperature as shown in Table 1 in an argon gas atmosphere having a purity of 99.9 vol%, and after 2 hours, the specimens were removed. Each specimen was collected such that the longitudinal direction of the specimen was parallel to the rolling surface and perpendicular to the rolling direction, and the conductivity at 20 °C was measured by the four-terminal method in accordance with JIS H 0505.

[Strength Stability During Heat Treatment]

[0053] Twenty samples each having a width of 50 mm and a length of 150 mm were collected from the above specimens, stacked and fixed with a copper wire, and placed in a furnace set to the peak aging temperature (see Table 1) in an argon atmosphere having a purity of 99.9% or more, and removed after 2 hours. Subsequently, in order to confirm the reproducibility, the same annealing was performed at another timing. The tensile strength of each of these specimens was investigated in the direction parallel to the rolling surface and perpendicular to the rolling direction according to JIS Z 2241 (2011) using a tensile tester to obtain the maximum, minimum and average value of the tensile strength. The following A and B were calculated: $A (\%) = \{(\text{maximum value} - \text{average value}) / \text{average value}\} \times 100$; and $B (\%) = \{(\text{average value} - \text{minimum value}) / \text{average value}\} \times 100$. A case where each of the above A and B was 5% or less was evaluated as "◎", and a case where any one of the above A and B was not within 5%, but each of the above A and B was 10% or less, was evaluated as "○", and other cases were evaluated as "x". Here, the "◎" was determined to be excellent in strength stability during the heat treatment, the "○" was determined to be good in strength stability during the heat treatment, and the "x" was determined to be poor in strength stability during the heat treatment.

[Discoloration Resistance During Heat Treatment]

[0054] A degree of discoloration was evaluated by evaluating the solder wettability after pickling with dilute sulfuric acid after the heat treatment for 2 hours at the peak aging temperature in an atmosphere of argon gas having a purity of 99.9 vol% or more. Using a solder checker (SAT-5200) from RHESCA CO., LTD., a mixed solution of 25 vol% of rosin and 75 vol% of ethanol was used as a flux. Each specimen was cut into a width of 10 mm and a length of 30 mm such that the rolling perpendicular direction was the longitudinal direction to obtain a sample, which was then immersed in 10 vol% dilute sulfuric acid for 10 seconds as a pretreatment, washed with water and dried. Used as a solder bath was a molten solder bath in which Sn-3% by mass Ag-0.5% by mass Cu was dissolved and maintained at 245 °C. One end of the sample in the longitudinal direction was immersed in the solder bath under conditions of an immersion rate of 5 mm/s, an immersion depth of 12 mm, and an immersion time of 10 seconds, and the wetting height after the solder wetting test was measured. A case where the wetting height was 12 mm or more was evaluated as "◎", a case where it was 6 mm or more was evaluated as "○", and a case where it was less than 6 mm was evaluated as "x". Here, the "◎" was determined to be excellent in the discoloration resistance, the "○" was determined to be good in the discoloration resistance, and the "x" was determined to be poor in the discoloration resistance.

[0055] In addition, for Examples and Comparative Examples, when the solder wettability was "◎", no discoloration was visually observed in appearance color tone after the heat treatment (copper color), and when it was "○", for example, discoloration to light blue color was observed, and when it was "x", discoloration to silvery white or golden color was observed.

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Table 1:

	Alloy Composition		Solutionizing		Hot Rolling	
	Main Component [% by mass]	Sub Component [% by mass]	Material Temperature [°C]	Cooling Rate [°C/sec]	Rolling Ratio [%]	Initiation Temperature [°C]
Example 1	Cu-3.2%Ti	-	800	120	30	380
Example 2	Cu-2.1%Ti	-	775	100	25	400
Example 3	Cu-4.5%Ti	-	850	120	30	400
Example 4	Cu-3.2%Ti	0.2%Fe	800	120	30	390
Example 5	Cu-3.2%Ti	0.01%B	820	120	25	400
Example 6	Cu-3.2%Ti	0.1%Co-0.05%Mg-0.02%Si-0.03%Ni	895	120	25	400
Example 7	Cu-3.2%Ti	0.05%Cr-0.02%Zr-0.1%Mo-0.02%Mn-0.05%V	750	120	25	410
Example 8	Cu-3.2%Ti	0.1%P-0.05%Nb	800	290	25	400
Example 9	Cu-3.2%Ti	0.45%Mn	800	55	30	390
Example 10	Cu-3.2%Ti	-	800	200	65	400
Example 11	Cu-3.2%Ti	-	800	120	10	400
Example 12	Cu-3.2%Ti	-	800	160	25	365
Example 13	Cu-3.2%Ti	-	800	85	25	455
Comparative Example 1	Cu-4.8%Ti	-	Cracks occurred during hot rolling			
Comparative Example 2	Cu-1.8%Ti	-	800	120	25	310
Comparative Example 3	Cu-3.2%Ti	-	920	100	25	300
Comparative Example 4	Cu-3.2%Ti	-	740	150	25	290
Comparative Example 5	Cu-3.2%Ti	-	800	300	25	280
Comparative Example 6	Cu-3.2%Ti	-	800	>300 (Water Cooling)	30	300
Comparative Example 7	Cu-3.2%Ti	-	800	45	30	300
Comparative Example 8	Cu-3.2%Ti	-	800	120	75	300
Comparative Example 9	Cu-3.2%Ti	-	800	120	8	320
Comparative Example 10	Cu-3.2%Ti	-	800	120	25	350
Comparative Example 11	Cu-3.2%Ti	-	800	120	25	470
Comparative Example 12	Cu-3.2%Ti	-	800	120	Cold rolling was performed instead of hot rolling (rolling ratio: 25%)	

Table 2:

	After Heat Treatment (Rolling Perpendicular Direction)				Evaluation	
	Peak Aging Temperature [°C]	Tensile strength (TS_{max}) [MPa]	Lower Value of One of TS_1/TS_{max} and TS_2/TS_{max}	Conductivity [% IACS]	Strength Stability	Discoloration Resistance
Example 1	380	950	0.993	10	◎	◎
Example 2	400	815	0.994	17	◎	◎
Example 3	360	1060	0.995	9.5	◎	◎
Example 4	360	1000	0.993	9.5	◎	◎
Example 5	380	950	0.995	10.5	◎	◎
Example 6	360	810	0.995	10.5	◎	◎
Example 7	380	850	0.982	14.2	○	◎
Example 8	420	980	0.994	16	◎	○
Example 9	360	1020	0.985	19.4	○	◎
Example 10	340	1180	0.982	12.5	○	◎
Example 11	400	810	0.993	9.8	◎	◎
Example 12	420	980	0.995	8.1	◎	○
Example 13	380	950	0.985	12.3	○	◎
Comparative Example 1	-	-	-	-	-	-
Comparative Example 2	400	780	0.995	16	◎	◎
Comparative Example 3	400	760	0.995	12	◎	◎
Comparative Example 4	400	860	0.971	16	×	◎
Comparative Example 5	480	980	0.994	18	◎	×
Comparative Example 6	480	880	0.985	19	◎	×
Comparative Example 7	380	1020	0.965	22	×	◎
Comparative Example 8	320	1240	0.961	14	×	◎
Comparative Example 9	420	740	0.985	12	◎	◎
Comparative Example 10	460	920	0.989	7.8	◎	×
Comparative Example 11	380	950	0.951	9.8	×	◎
Comparative Example 12	460	940	0.968	12	×	×

[Results]

[0056] As described above, each titanium copper plate of each Example and Each Comparative Example was produced as a specimen under each condition as shown in Table 1. As a result, it was found that each titanium copper plate had the characteristics as shown in Table 2. Thus, each titanium copper obtained in Examples 1 to 13 had a peak aging temperature of 420 °C or less after the heat treatment, and had a TS_{max} of from 800 to 1200 MPa in the rolling perpendicular direction after the heat treatment, and further had ratios: TS_1 / TS_{max} and TS_2 / TS_{max} of 0.98 or more, respectively, whereby the strength stability and discoloration resistance after the heat treatment were excellent. Further, it was found that the titanium copper obtained in each of Examples 1 to 13 could be produced by carrying out the solutionizing treatment and the hot finish rolling on titanium copper having the above composition under each of the above conditions.

[0057] In Comparative Example 1, the hot rolling ratio was significantly poor and the step could not proceed, because the Ti concentration was higher.

[0058] In Comparative Example 2, the tensile strength after the heat treatment was lower, because the Ti concentration was less than 2.0% by mass.

[0059] In Comparative Example 3, the tensile strength after the heat treatment was lower, because the solutionizing temperature was higher.

[0060] In Comparative Example 4, the ratios TS_1 / TS_{max} and TS_2 / TS_{max} were lower, and the strength stability after the heat treatment was poor, because the solutionizing temperature was lower.

[0061] In Comparative Examples 5 and 6, the peak aging temperature was higher and the discoloration resistance was deteriorated, because the cooling rate at the time of solutionizing was higher.

[0062] In Comparative Example 7, the ratios TS_1 / TS_{max} and TS_2 / TS_{max} were lower, and the strength stability after the heat treatment was poor, because the cooling rate at the time of solutionizing was lower.

[0063] In Comparative Example 8, the TS_{max} was 1200 MPa or more, and the ratios TS_1 / TS_{max} and TS_2 / TS_{max} were lower, and the strength stability after the heat treatment was poor, because the hot rolling ratio was higher.

[0064] In Comparative Example 9, the TS_{max} was less than 800 MPa, because the hot rolling ratio was lower.

[0065] In Comparative Example 10, the peak aging temperature was 420 °C or more, the discoloration resistance was deteriorated, and the conductivity was lower, because the material temperature at the initiation of the hot rolling was lower.

[0066] In Comparative Example 11, the ratios TS_1 / TS_{max} and TS_2 / TS_{max} were lower, and the strength stability after the heat treatment was poor, because the material temperature at the initiation of the hot rolling was higher.

[0067] In Comparative Example 12, the discoloration resistance was poor due to the higher peak aging temperature, and the strength stability after the heat treatment was poor due to the lower TS_1 / TS_{max} and TS_2 / TS_{max} , because the hot rolling was not carried out.

Claims

1. A titanium copper plate, the titanium copper plate containing from 2.0 to 4.5% by mass of Ti, the balance being copper and inevitable impurities, wherein a peak aging temperature at which a maximum value (TS_{max}) of a tensile strength in a direction parallel to a rolling surface and perpendicular to a rolling direction is obtained is 420 °C or less, and the TS_{max} is from 800 to 1200 MPa, wherein a ratio (TS_1 / TS_{max}) of a tensile strength TS_1 in the perpendicular direction after a heat treatment at a temperature which is higher by 20 °C than the peak aging temperature to the TS_{max} is 0.98 or more, and wherein a ratio (TS_2 / TS_{max}) of a tensile strength TS_2 in the perpendicular direction after the heat treatment at a temperature which is lower by 20 °C than the peak aging temperature for 2 hours to the TS_{max} is 0.98 or more.
2. The titanium copper plate according to claim 1, wherein the ratio: TS_1 / TS_{max} is 0.99 or more, and the ratio: TS_2 / TS_{max} is 0.99 or more.
3. The titanium copper plate according to claim 1 or 2, wherein the TS_{max} is from 800 to 1100 MPa.
4. The titanium copper plate according to any one of claims 1 to 3, wherein the titanium copper plate has a conductivity of from 8 to 20% IACS after the heat treatment at the peak aging temperature for 2 hours.
5. The titanium copper plate according to any one of claims 1 to 4, further comprising at least one third element selected from the group consisting of Fe, Co, Mg, Si, Ni, Cr, Zr, Mo, V, Nb, Mn, B, and P in a total amount of 0.5% by mass or less.
6. A pressed product, comprising the titanium copper plate according to any one of claims 1 to 5.
7. A method for manufacturing a pressed product, comprising subjecting the titanium copper plate according to any one of claims 1 to 5 to pressing and an aging treatment in this order.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/021864

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C22C9/00 (2006.01) i, C22F1/08 (2006.01) i, C22F1/00 (2006.01) n

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. C22C9/00, C22F1/08, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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.
A	JP 2002-356726 A (NIPPON MINING & METALS CO., LTD.) 13 December 2002, & US 2002/0157741 A1 & US 2010/0276037 A1 & KR 10-2002-0068283 A & CN 1384216 A	1-7
A	WO 2007/015549 A1 (NIPPON MINING & METALS CO., LTD.) 08 February 2007, & US 2010/0101687 A1 & CN 101238230 A & KR 10-2008-0027910 A & TW 200730643 A	1-7
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Date of the actual completion of the international search
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