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

(57) Provided is 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 good springiness and dimensional stability after the 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 the titanium copper plate has a tensile strength in a rolling parallel direction of 750

MPa or more, and a conductivity of from 4.0 to 8.0% IACS, and wherein the titanium copper plate has a spring limit value of 800 MPa or more in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours, and a thermal expansion/contraction ratio of 100 ppm or less in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours.

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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] On the other hand, 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 (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).

[0007] Claim 16 of Patent Literature 5 mentions that an aging treatment (hereinafter referred to as a heat treatment) carried out after pressing results in titanium copper having a hardness of 345 Hv or more after the heat treatment. However, the titanium copper has a large dimensional change after the heat treatment and poor stability. Particularly, Examples (Nos. 1 to 10, 12, 14 to 16) in Table 10 of Patent Literature 5 show that an amount of thermal expansion/contraction in a direction parallel to the rolling direction after the heat treatment is larger, i.e., 0.05% (500 ppm) or more.

[0008] Therefore, in an aspect, 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 good springiness and dimensional stability after the heat treatment.

Solution to Problem

[0009] As a results of intensive studies for the springiness and dimensional stability after the heat treatment and the characteristics of titanium copper in order to solve the above problems, the present inventors have found that titanium copper having controlled tensile strength and conductivity before the heat treatment has an improved spring limit value and improved thermal expansion/contraction properties after the heat treatment, and that the titanium copper is obtained by solutionizing treatment conditions, a temperature of hot rolling and a rolling workability, which will be described later, and they have arrived at the present invention.

[0010] 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 the titanium copper plate has a tensile strength in a rolling parallel direction of 750 MPa or more, and a conductivity of from 4.0 to 8.0% IACS, and wherein the titanium copper plate has a spring limit value of 800 MPa or more in a rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours, and a thermal expansion/contraction ratio of 100 ppm or less in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours.

[0011] In one embodiment of the titanium copper plate according to the present invention, the conductivity is from 4.0 to 6.0% IACS.

[0012] In one embodiment of the titanium copper plate according to the present invention, the spring limit value is 850 MPa or more.

[0013] In one embodiment of the titanium copper plate according to the present invention, the sum of the thermal expansion/contraction ratio in the rolling parallel direction and the thermal expansion/contraction ratio in a rolling perpendicular direction which is a direction parallel to a rolling surface and orthogonal to the rolling parallel direction is 200 ppm or less, after the heat treatment at 400 °C for 2 hours.

[0014] In one embodiment of the titanium copper plate according to the present invention, a ratio of a minimum bend radius (MBR) to a thickness (t) is $MBR / t \leq 2.0$, in a W bending test wherein a bending axis is parallel to the rolling direction (BW direction).

[0015] In one embodiment of the titanium copper plate according to the present invention, the ratio is $MBR / t \leq 1.8$.

[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 any one of the above titanium copper plates.

[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 springiness and dimensional stability after a heat treatment. Since the titanium copper plate according to the present invention has improved spring limit value and thermal expansion/contraction properties after the heat treatment, it can be suitably used for the production of small electronic components manufactured by bending and subsequent heat treatment, which have good product dimensions and springiness.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is a view illustrating a sample for measuring a thermal contraction rate.

DETAILED DESCRIPTION OF THE INVENTION

[0021] 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]

[0022] In an embodiment, the present invention provides a titanium copper plate containing from 2.0 to 4.5% by mass of Ti, the balance being copper and inevitable impurities, wherein the titanium copper plate has a tensile strength in a rolling parallel direction of 750 MPa or more, and a conductivity of from 4.0 to 8.0% IACS, and wherein the titanium copper plate has a spring limit value of 800 MPa or more in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours, and a thermal expansion/contraction ratio of 100 ppm or less in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours. Hereinafter, preferable embodiments of each component will be described.

(Ti Content)

[0023] In an embodiment of the titanium copper plate according to the present invention, the desired Ti content leads to solid solution of Ti in the Cu matrix by a solutionizing treatment, and to dispersion of fine precipitates in the alloy by an aging treatment, thereby increasing the strength. That is, the Ti content is 2.0% by mass or more, and preferably 2.5% by mass or more, and more preferably 3.0% by mass or more, from the viewpoint that the tensile strength in the rolling parallel direction before the heat treatment is 750 MPa or more and a sufficient spring limit value is obtained after the heat treatment. Further, it is 4.5% by mass or less, and preferably 3.5% by mass or less, and more preferably 3.3% by mass or less, in terms of suppressing any breakage of the material in hot rolling and further improving a bendability.

(Third Element)

[0024] 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.

[0025] 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)

[0026] 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.

(Tensile Strength)

[0027] In the present invention, when the tensile strength of the titanium copper plate is 750 MPa or more in the rolling parallel direction and the conductivity shown below is satisfied, a desired spring limit value can be obtained when subjected to the heat treatment at 400 °C for 2 hours. It is preferably 775 MPa or more, and more preferably 800 MPa or more. However, although no upper limit is set, the tensile strength is preferably less than 900 MPa in terms of maintaining the dimensional stability of the product without excessive spring-back. On the other hand, when the tensile strength is lower than 750 MPa, the spring limit value after the heat treatment will be lower, so that the springiness tends to decrease.

[0028] It should be noted that the tensile strength is measured using a tensile tester in accordance with JIS Z 2241 (2011).

(Conductivity)

[0029] In an embodiment, the titanium copper plate according to the present invention provides the desired thermal expansion/contraction ratio and spring limit value when subjected to the heat treatment at 400 °C for 2 hours, for the reason that a balance of aging precipitation is optimized if the titanium copper plate satisfies the desired tensile strength as described above and has a conductivity of from 4.0 to 8.0% IACS. It is preferably from 4.0 to 7.0% IACS, and more preferably from 4.0 to 6.0% IACS. When the conductivity is lower than 4.0% IACS, the tensile strength may tend to be decreased, and the spring limit value after the heat treatment may be decreased. On the other hand, if the conductivity is higher than 8.0% IACS, the spring limit value after the heat treatment may tend to be decreased.

[0030] It should be noted that the conductivity is measured in accordance with JIS H 0505.

(Thermal Expansion/Contraction Ratio)

[0031] The dimensional change due to the heat treatment is caused by the balance among changes in thermal expansion/contraction in a rolling parallel direction after the heat treatment, a rolling perpendicular direction which is a direction parallel to a rolling surface and orthogonal to the rolling direction, and in a thickness direction. It can be generally evaluated by the dimensional change in the rolling parallel direction when subjected to the heat treatment at 400 °C for 2 hours. The thermal expansion/contraction ratio in the rolling parallel direction is preferably 100 ppm or less, and more preferably 90 ppm or less, and still more preferably 60 ppm or less, from the viewpoint that the dimensional change of the product after the heat treatment is lower and better. Here, the reason why the heating condition for measuring the thermal expansion/contraction ratio is 400 °C for 2 hours is that the strength of the titanium copper plate tends to be the highest when measured under this condition. The lower limit of the thermal expansion/contraction ratio is not limited in terms of characteristics of the titanium copper plate, but the thermal expansion/contraction ratio is not usually less than 1 ppm.

[0032] Further, the dimensional change in the rolling perpendicular direction orthogonal to the rolling direction when subjected to the heat treatment at 400 °C for 2 hours is measured to calculate the sum of the thermal expansion/contraction ratio in the rolling parallel direction and the thermal expansion/contraction ratio in the rolling perpendicular direction. In this case, if the sum of the thermal expansion/contraction ratio in the rolling parallel direction and the thermal expansion/contraction ratio in the rolling perpendicular direction after the heat treatment at 400 °C for 2 hours is 200 ppm or less, the dimensional stability after the heat treatment is further improved, which is preferably 150 ppm or less, and more preferably 100 ppm or less. However, it is more preferable that the sum of the thermal expansion/contraction ratios is lower.

[0033] It should be noted that the thermal expansion/contraction ratio is measured as follows:

Samples of the titanium copper plate are collected such that a longitudinal direction of each sample is parallel to the rolling direction. Further, the other samples of the titanium copper plate are collected in the rolling perpendicular direction in which the longitudinal direction of each is orthogonal to the thickness. Subsequently, as shown in FIG. 1, two dents are stamped at a predetermined interval (L_0). The samples in the rolling parallel direction and the rolling perpendicular direction are then heated under predetermined conditions, and dent interval (L) after heating is measured.

(Bendability)

[0034] The bendability is evaluated by a W bending test (JIS H 3130 (2012)) using a strip-shaped sample having a width of 10 mm and a length of 30 mm. A collecting direction of the sample is a direction in which a bending axis is parallel to the rolling direction (BW direction), and the evaluation is carried out at a ratio MBR / t of a minimum bend radius MBR (Minimum Bend Radius) at which cracks do not occur to the thickness t . The ratio (MBR / t) of the minimum

bend radius (MBR) is preferably 2.0 or less in terms of ensuring good bendability. A more preferred range of the MBR / t is 1.8 or less.

[0035] It should be noted that the bendability is measured in accordance with JIS H 3130 (2012).

5 (Spring Limit Value)

[0036] The spring limit value of the titanium copper plate is measured after the heat treatment at 400 °C for 2 hours. It is believed that the spring limit value of 800 MPa or more is sufficient to satisfy the springiness for use in connectors. Although the upper limit is not particularly set, it is preferably 825 MPa or more, and more preferably 850 MPa or more.

10 **[0037]** As a method for measuring the spring limit value, a moment type test defined in JIS H 3130 (2012) is conducted.

[2. Method for Manufacturing Titanium Copper Plate]

15 **[0038]** 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.

20 Further, in order to increase the strength, cold rolling may be carried out after the solutionizing treatment.

[0039] The titanium copper plate according to the present invention can be manufactured by carrying out, in particular, the solutionizing treatment and a finish rolling (hot rolling) step immediately after the solutionizing treatment, under appropriate conditions. Hereinafter, suitable production examples will be sequentially described for each step.

25 1) Production of Ingot

[0040] 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

40 **[0041]** 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

50 **[0042]** The solutionizing treatment is preferably carried out after repeating the cold rolling and annealing as needed. In the present invention, a temperature of solutionizing is preferably 750 °C or more, and more preferably 775 °C or more, and even more preferably 790 °C or more, in terms of adjusting the conductivity to a suitable range and improving the spring limit value after the heat treatment. On the other hand, the temperature of solutionizing is preferably 900 °C or less, and more preferably 875 °C or less, and further preferably 850 °C or less, from the viewpoints that the metal structure will be dense, the tensile strength is higher, and the bendability is better. A temperature rising rate at this time is preferably as fast as possible.

[0043] Further, in an embodiment, the solutionizing time is preferably from 5 seconds to 30 minutes, and more preferably from 10 seconds to 5 minutes, in order to perform the solutionizing treatment sufficiently.

[0044] On the other hand, the cooling after the solutionizing treatment is preferably water cooling. In a preferred

embodiment, for example, an average cooling rate is preferably 150 °C/sec or more, and more preferably 155 °C/sec or more. If the average cooling rate is less than 150 °C/sec, precipitation occurs during cooling, so that the conductivity may be increased and the spring limit value after the heat treatment may be decreased. On the other hand, although the upper limit of the cooling rate is not set, the water cooling is sufficient to have the required cooling rate. However, from the viewpoint of sufficiently obtaining the effect of increasing the strength, the average cooling rate is preferably 1500 °C/sec or less. The conductivity after the solutionizing can be adjusted to a range of from 2.0 to 5.0% IACS. As used herein, the average cooling rate refers to a value (°C/sec) obtained by measuring a time (cooling time) required for cooling from 750 °C at the start of the cooling to 100 °C, and calculating the value by the equation: $(750 - 100) (°C) / \text{cooling time (seconds)}$.

4) Finish Rolling

[0045] 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 50% or less, and preferably 40% or less, in terms of obtaining a suitable thermal expansion/contraction ratio, and more preferably 35% or less in terms of further improvement of bendability. However, it is 15% or more, and preferably 20% or more, and more preferably 25% or more, in terms of providing the tensile strength in the preferable range and increasing the spring limit value after the heat treatment. The workability is defined by $\{((\text{thickness before rolling} - \text{thickness after rolling}) / \text{thickness before rolling}) \times 100\%$.

[0046] 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 250 to 350 °C, and Ti that has undergone the solid solution by the solutionizing forms nuclei required for precipitation due to the hot rolling. There is no problem if the initiation temperature of the hot rolling is lower than the solutionizing temperature, and it is important to control the material temperature at the end of the hot rolling.

[0047] The hot rolling temperature is preferably 250 °C or more, and more preferably 280 °C or more, and even more preferably 300 °C or more, from the viewpoints that because the conductivity after rolling is 4.0% IACS or more, the thermal expansion/contraction ratio in the rolling parallel direction after the heat treatment at 400 °C for 2 hours is 100 ppm or less, and the spring limit value after the heat treatment is further increased. However, the hot rolling temperature is preferably 350 °C or less, and more preferably 330 °C or less, and even more preferably 320 °C or less, from the viewpoints that any excessive nucleation of precipitation does not occur, any excessive precipitation of a Cu-Ti compound does not occur, the conductivity is not increased, and the spring limit value after the heat treatment is suppressed. By the hot rolling temperature in such a suitable range, the sum of the thermal expansion/contraction ratios in the rolling parallel direction and in the rolling perpendicular direction which is parallel to the rolling surface and orthogonal to the rolling direction after the heat treatment at 400 °C for 2 hours will be 200 ppm or more.

[0048] It is preferable to adjust the above conditions such that the conductivity after the hot rolling is in the range of from 4.0 to 8.0% IACS. Although the present invention is not particularly limited, the Cu-Ti compound is precipitated by the heat treatment of the above material after pressing, and a change in a lattice constant of titanium copper due to the precipitation may be affected on the thermal expansion/contraction ratio. It is believed that by the hot rolling step suppresses an amount of precipitation after pressing, resulting in a decreased amount of thermal expansion/contraction.

[0049] 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]

[0050] The titanium copper plate manufactured by the manufacturing method as described above is subjected to pressing by a press maker and an aging treatment 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 300 to 440 °C so as to have improved spring limit value and dimensional stability of the material after the treatment. Further, a time of the aging treatment may preferably be from 0.5 to 10 hours. The pressed product includes the titanium copper plate as described above.

EXAMPLES

[0051] 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 Plate]

[0052] When the titanium copper plates of Examples 1 to 15 and Comparative Examples 1 to 9 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.

[0053] First, electrolytic copper was melted in a vacuum melting furnace, Ti was added so as to have each Ti concentration as shown in Table 1 according to Examples 1 to 15 and Comparative Examples 1 to 9, and optionally the third element was further added at the concentration as shown in Table 1 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. It should be noted that the figure of each component as shown in the table indicates % by mass.

[0054] After descaling by face cutting, a plate having a thickness of 0.25 mm was then obtained by cold rolling. The solutionizing treatment was then carried out for 10 minutes under the conditions as shown in Table 1, and water cooling was then carried out. More specifically, a sample and a thermocouple were inserted into an electric furnace conditioned at 700 to 1000 °C in the solutionizing treatment, the material temperature was measured with the thermocouple, and the sample was removed at the time when the material temperature reached 700 to 1000 °C, and placed in a water tank (25 °C) or a furnace that was maintained at a predetermined temperature to cool the sample. The cooling rate (°C/sec) except for the water cooling was determined from the cooling time from the reaching temperature of the material to the final temperature of 100 °C for the material temperature. After descaling by washing with an acid, as final rolling, the hot rolling (a thickness of 0.15 mm) was then carried out while adjusting the workability and material temperature at the end as shown in Table 1 to obtain samples of Examples 1 to 15 and Comparative Examples 1 to 9.

[0055] Each sample treated as described above was characterized under the following conditions:

[Component Composition]

[0056] The alloy element concentration of each material after strain relief annealing was analyzed by ICP-mass spectrometry. As a result, it was substantially the same as the composition ratio of the added elements.

[Tensile Strength]

[0057] The tensile strength was measured using a tensile tester such that the longitudinal direction of each sample was parallel to the rolling direction, according to JIS Z 2241 (2011).

[Conductivity]

[0058] Each sample was collected such that the longitudinal direction of the sample was parallel to the rolling direction, and the conductivity at 20 °C was measured by the four-terminal method in accordance with JIS H 0505.

[Bendability]

[0059] The bendability of each sample finally obtained was evaluated by measuring a MBR / t value, a ratio of the minimum bend radius (MBR) at which cracks did not occur, to the thickness (t), by a Badway (bending axis in the same direction as the rolling direction) W bending test according to JIS H 3130 (2012).

[Thermal Expansion/Contraction Ratio]

[0060] From the material after the hot rolling, strip-shaped samples each having a width of 20 mm and a length of 210 mm were collected such that the longitudinal direction of each sample was parallel to the rolling direction. Further, other samples were collected in the rolling perpendicular direction where the longitudinal direction of each sample was orthogonal to the thickness. Subsequently, as shown in FIG. 1, two dents were stamped at an interval L_0 (= 200 mm). Each of the samples in the rolling parallel direction and the rolling perpendicular direction was heated at 400 °C for 2 hours, and the dent interval (L) after heating was measured. Subsequently, as the thermal expansion/contraction ratio (ppm), an absolute value of the value calculated by the equation: $(L - L_0) / L_0 \times 10^6$ was determined. Further, the sum of the thermal expansion/contraction ratio in the rolling parallel direction and the thermal expansion/contraction ratio in the rolling perpendicular direction was determined.

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[Spring Limit Value]

[0061] After heating the material after the hot rolling at 400 °C for 2 hours, the spring limit value in the rolling perpendicular direction was determined in accordance with a moment type test defined in JIS H 3130 (2012) by holding each long strip-shaped sample (a width of each sample of 10 mm) in a cantilevered manner such that the longitudinal direction of each sample was parallel to the rolling direction, and measuring the maximum surface stress from a bending moment that generated permanent deflection defined by the thickness of the material.

[0062] The test was conducted under conditions of a thickness t (mm) of the material, a distance from the fixed end of the material to the load point of 1 (mm), and for the permanent deflection δ (mm), with $l^2 = 4000 t$ and $\delta = 0.1$.

[Dimensional Stability]

[0063] As a bending angle before the heat treatment, an actual bending deformation angle θ of the bent portion was determined after carrying out the W bending on the material after the hot rolling in a range where bending cracks did not occur. When the bending direction was Goodway (the direction where the bending axis was orthogonal to the rolling direction) and the thickness (t) was 0.15 mm, the bending condition was $R / t = 3.3$. However, any bending R may be used as long as bending cracks do not occur. Further, as a bending angle after the heat treatment, a bending deformation angle θ' was determined by heating each sample at 400 °C for 2 hours and then carrying out the same bending.

[0064] Thus, an absolute value of a bending angle change " $\theta' - \theta$ " before and after the heat treatment was calculated. In Table 1, a value of less than 0.5° was designated as "◎", a value of 0.5° or more and less than 1.0° was designated as "○", and a value of 1.0° or more was designated as "×". It can be determined that "◎" is excellent in dimensional stability after the heat treatment, "○" is good in dimensional stability after the heat treatment, and "×" is poor in dimensional stability after the heat treatment.

Table 1:

	Alloy Composition		Solutionizing		Hot Rolling		Before Heat Treatment			After Heat Treatment (400 °C, 2 hours)			
	Main Component (% by mass)	Sub Component (% by mass)	Material Temperature (°C)	Cooling Rate (°C/sec)	Workability (%)	End Temperature (°C)	Tensile Strength (MPa)	Conductivity (%IACS)	Bendability (MBRA)	Thermal Expansion/Contraction Ratio in Rolling Parallel Direction (ppm)	Sum of Thermal Expansion/Contraction ratios in Rolling parallel Direction and Rolling Perpendicular Direction (ppm)	Spring Limit Value (MPa)	Dimensional Stability
Example 1	Cu-32%Ti		800	300 (Water Cooling)	25	305	850	4.3	1.0	50	95	880	○
Example 2	Cu-21%Ti		775	300 (Water Cooling)	25	300	760	5.9	0	35	85	810	○
Example 3	Cu-4.5%Ti		850	300 (Water Cooling)	25	280	1020	4.6	2.0	55	120	1050	○
Example 4	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	25	320	880	42	0.8	50	90	900	○
Example 5	Cu-3.2%Ti	0.01%B	820	300 (Water Cooling)	25	310	890	5.3	1.1	60	110	910	○
Example 6	Cu-3.2%Ti	0.1%Co-0.05%Mg-0.02%Si-0.03Ni	895	300 (Water Cooling)	25	300	760	4.1	1.7	90	140	810	○

(continued)

	Alloy Composition		Solutionizing		Hot Rolling		Before Heat Treatment			After Heat Treatment (400 °C, 2 hours)			
	Main Component (% by mass)	Sub Component (% by mass)	Material Temperature (°C)	Cooling Rate (°C/sec)	Workability (%)	End Temperature (°C)	Tensile Strength (MPa)	Conductivity (%IACS)	Bendability (MBRA)	Thermal Expansion/Contraction Ratio in Rolling Parallel Direction (ppm)	Sum of Thermal Expansion/Contraction ratios in Rolling parallel Direction and Rolling Perpendicular Direction (ppm)	Spring Limit Value (MPa)	Dimensional Stability
Example 7	Cu-3.2%Ti	0.05%Cr-0.02%Zr-0.1%Mo-0.02%Mn-0.05%V	750	300 (Water Cooling)	25	305	880	7.8	1.3	55	100	805	○
Example 8	Cu-3.2%Ti	0.1%P-0.05%Nb	800	155	25	310	890	72	1.2	45	145	820	○
Example 9	Cu-3.2%Ti	-	800	300 (Water Cooling)	50	290	980	4.2	2.3	95	145	990	○
Example 10	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	35	320	870	4.2	1.8	57	102	920	○
Example 11	Cu-3.2*Ti	0.3%Fe	800	300 (Water Cooling)	15	310	770	4.3	0.5	20	75	810	○
Example 12	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	25	345	820	78	1.0	60	180	830	○
Example 13	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	25	255	765	4.2	0.5	85	140	820	○

(continued)

	Alloy Composition		Solutionizing		Hot Rolling		Before Heat Treatment			After Heat Treatment (400 °C, 2 hours)			
	Main Component (% by mass)	Sub Component (% by mass)	Material Temperature (°C)	Cooling Rate (°C/sec)	Workability (%)	End Temperature (°C)	Tensile Strength (MPa)	Conductivity (%IACS)	Bendability (MBRA)	Thermal Expansion/Contraction Ratio in Rolling Parallel Direction (ppm)	Sum of Thermal Expansion/Contraction ratios in Rolling parallel Direction and Rolling Perpendicular Direction (ppm)	Spring Limit Value (MPa)	Dimensional Stability
Example 14	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	25	355	830	7.9	1.5	60	210	850	○
Example 15	Cu-3.2%Ti	0.2%Fe	800	300 (Water Cooling)	45	355	830	7.8	2.2	95	210	830	○
Comparative Example 1	Cu-4.8%Ti	-	Cracks occurred during hot rolling										
Comparative Example 2	Cu-1.8%Ti	-	800	300 (Water Cooling)	25	310	740	4.2	0	30	60	750	○
Comparative Example 3	Cu-3.2%Ti	-	920	300 (Water Cooling)	25	300	735	4.5	3.1	210	310	755	×
Comparative Example 4	Cu-3.3%Ti	-	740	300 (Water Cooling)	25	290	810	8.3	1.9	70	130	760	○
Comparative Example 5	Cu-3.2%Ti	-	800	140	25	280	870	8.4	1.5	70	135	770	○

(continued)

	Alloy Composition		Solutionizing		Hot Rolling		Before Heat Treatment			After Heat Treatment (400 °C, 2 hours)			
	Main Component (% by mass)	Sub Component (% by mass)	Material Temperature (°C)	Cooling Rate (°C/sec)	Workability (%)	End Temperature (°C)	Tensile Strength (MPa)	Conductivity (%IACS)	Bendability (MBRA)	Thermal Expansion/Contraction Ratio in Rolling Parallel Direction (ppm)	Sum of Thermal Expansion/Contraction ratios in Rolling parallel Direction and Rolling Perpendicular Direction (ppm)	Spring Limit Value (MPa)	Dimensional Stability
Comparative Example 6	Cu-3.2%Ti	-	800	300 (Water Cooling)	60	300	1050	53	2.5	112	165	1020	×
Comparative Example 7	Cu-3.2%Ti	-	800	300 (Water Cooling)	12	320	732	4.3	1.2	3.8	85	788	○
Comparative Example 8	Cu-3.2%Ti	-	800	300 (Water Cooling)	25	360	870	8.5	1.9	85	230	720	×
Comparative Example 9	Cu-3.2%Ti	-	800	300 (Water Cooling)	25	245	870	3.8	1.1	131	200	770	×
Reference Example 1	C1720-1/4H		-	-	-	-	570	17	0	260	350	870	×
Reference Example 2	C1720-1/4H		-	-	-	-	570	17	0	180	280	1080	×

[Results]

[0065] As described above, titanium copper of each Example and Each Comparative Example was produced as a sample under each condition as shown in Table 1. As a result, it was found that each titanium copper had the characteristics as shown in Table 1. Thus, the titanium copper plated of each of Examples 1 to 15 had the tensile strength and conductivity as described above, and had excellent springiness and dimensional stability after the heat treatment at 400 °C for 2 hours. Further, it was found that the titanium copper plate of each of Examples 1 to 15 could be produced by carrying out hot rolling, intermediate rolling, solutionizing treatment, and hot finish rolling on titanium copper having the above composition under each of the above conditions.

[0066] Further, Examples 1, 3 to 7, and 10 to 14 had excellent bendability in addition to the excellent spring limit value and thermal expansion/contraction ratio, because the finish workability after the hot rolling was 35% or less.

[0067] Further, as reference examples, a commercially available Cu-Be alloy (C1720-1/4H (from NGK INSULATORS, LTD.)) is shown. For the aging temperature of 400 °C (Reference Example 1) and the recommended aging temperature of the Cu-Be alloy of 315 °C (Reference Example 2), the titanium copper plate of each of Examples 1, 3 to 5, 9, and 10 had the spring limit value equivalent to that of the Cu-Be alloy, as well as the significantly improved thermal expansion/contraction characteristics.

[0068] In Comparative Example 1, the hot workability was significantly poor and the step could not proceed, because the Ti concentration was higher.

[0069] In Comparative Example 2, the tensile strength after the hot rolling was lower and the spring limit value after the heat treatment was poor, because the Ti concentration was less than 2.0%.

[0070] In Comparative Example 3, the tensile strength after the finish rolling was lower because the solutionizing temperature was higher, and the dimensional change and the spring limit value were poor because the thermal expansion/contraction ratio after the heat treatment was higher.

[0071] In Comparative Example 4, the conductivity after the hot rolling was higher and the spring limit value was poor, because the solutionizing temperature was lower.

[0072] In Comparative Example 5, the conductivity after the hot rolling was higher and the spring limit value was poor, because the cooling rate during the solutionizing was lower.

[0073] In Comparative Example 6, the thermal expansion/contraction ratio after the heat treatment was higher, and the dimensional stability was deteriorated, because the hot rolling workability was higher.

[0074] In Comparative Example 7, the tensile strength was lower and the spring limit value after the heat treatment was poor, because the hot rolling workability was lower.

[0075] In Comparative Example 8, the conductivity after the hot rolling was higher and the spring limit value after the heat treatment was poor, because the hot rolling temperature was higher.

[0076] In Comparative Example 9, the thermal expansion/contraction ratio after the heat treatment was higher because the hot rolling temperature was lower and the conductivity after the hot rolling was lower, resulting in poor dimensional stability, and the spring limit value was poor because there were few precipitation nuclei during the heat treatment.

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 the titanium copper plate has a tensile strength in a rolling parallel direction of 750 MPa or more, and a conductivity of from 4.0 to 8.0% IACS, and wherein the titanium copper plate has a spring limit value of 800 MPa or more in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours, and a thermal expansion/contraction ratio of 100 ppm or less in the rolling parallel direction when subjected to a heat treatment at 400 °C for 2 hours.

2. The titanium copper plate according to claim 1, wherein the conductivity is from 4.0 to 6.0% IACS.

3. The titanium copper plate according to claim 1 or 2, wherein the spring limit value is 850 MPa or more.

4. The titanium copper plate according to any one of claims 1 to 3, wherein the sum of the thermal expansion/contraction ratio in the rolling parallel direction and the thermal expansion/contraction ratio in a rolling perpendicular direction which is a direction parallel to a rolling surface and orthogonal to the rolling parallel direction is 200 ppm or less, after the heat treatment at 400 °C for 2 hours.

5. The titanium copper plate according to any one of claims 1 to 4, wherein a ratio of a minimum bend radius (MBR) to a thickness (t) is $MBR / t \leq 2.0$, in a W bending test wherein a bending axis is parallel to the rolling direction (BW)

direction).

6. The titanium copper plate according to claim 5, wherein the ratio is $MBR / t \leq 1.8$.

5 7. The titanium copper plate according to any one of claims 1 to 6, 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.

8. A pressed product, comprising the titanium copper plate according to any one of claims 1 to 7.

10 9. A method for manufacturing a pressed product, comprising subjecting the titanium copper plate according to any one of claims 1 to 7 to pressing and an aging treatment in this order.

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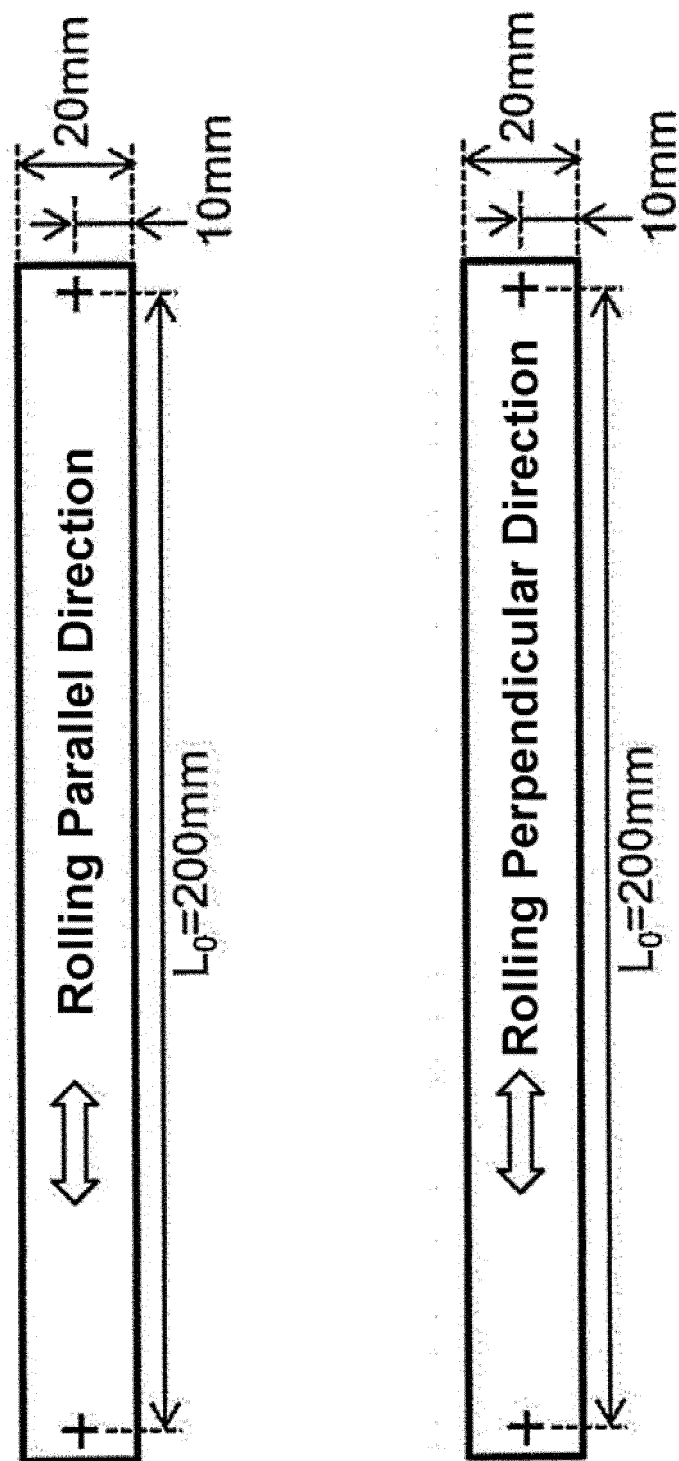


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/021863

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	1-9
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	1-9
A	JP 2005-344143 A (NIPPON MINING & METALS CO., LTD.) 15 December 2005, & US 2006/0011275 A1 & KR 10-2006-0046273 A & CN 1704492 A & TW 200602501 A	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search
30.07.2019Date of mailing of the international search report
13.08.2019

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