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(54) **TITANIUM COPPER FOR ELECTRONIC COMPONENTS**

(57) The present invention is intended to improve bending workability of titanium copper for electronic components, and to provide a titanium copper for electronic components, which has excellent bending workability even when subjected to beating process, and to provide a method for manufacturing the same. One embodiment of the present invention is a titanium copper, comprising 2.0 to 4.5 mass% of Ti, and at least one element selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B,

Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities, wherein in a crystal orientation analysis by EBSD measurement on the rolled surface, when an orientation difference of 5° or more is defined as a crystal grain boundary, a coefficient of variation of crystal grain size is 45% or less, and an area ratio of Cube orientation {001} <100> is 5% or less.

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Description**[Technical Field]**

[0001] The present invention is related to a titanium copper for electronic components which is suitable for electronic components, particularly connectors, battery terminals, jacks, relays, switches, autofocus camera modules, lead frames, and a method for manufacturing the titanium copper.

[Background Art]

[0002] In recent years, the miniaturization of electronic components such as lead frames, connectors which are used in electrical or electronic equipment and in-vehicle parts, has progressed, and there is a remarkable trend toward narrow pitch and low height for copper alloy members constituting electronic components. The smaller the connector is, the smaller the pin width is, and the smaller the folded work shape is. Therefore, the copper alloy members are required to have high strength to obtain the necessary spring characteristics. In this regard, a copper alloy containing titanium (hereinafter referred to as "titanium copper") has a relatively high strength and is excellent in stress relaxation characteristics among copper alloys. Therefore, titanium copper has been used for a long time as a material for signal terminals, whose strength is particularly required.

[0003] Titanium copper is an age hardening type copper alloy. When a supersaturated solid solution of Ti (which is a solute atom) is formed by the solution heat treatment, and heat treatment for a relatively long time at a low temperature is performed from this state, a modulation structure, in which the Ti concentration in the parent phase fluctuates periodically, develops and results into improvement of strength, because of spinodal decomposition. In the case, the problem is that the strength and the bending workability are contradictory properties. That is, if the strength is increased, the bending workability is impaired, and on the contrary, when emphasis is placed on the bending workability, the desired strength can not be obtained. In general, the higher the reduction ratio of cold rolling is, the larger the introduced amount of dislocation is, and the higher the dislocation density is. And thus, the number of nucleation sites contributing to precipitation increases, and the strength after aging treatment can be increased. However, when the reduction ratio is too high, the bending workability deteriorates. For This reason, it has been a problem to achieve both strength and bending workability.

[0004] Under this circumstance, Patent Document 1 (JP2013-100586A) discloses a titanium copper comprising Ti of 1.5 to 5.0 mass%, and the rest consisting of copper and inevitable impurities, having a tensile strength of 800 MPa or more, wherein when an EBSD measurement is carried out parallel to the plate thickness direction at the central portion in the plate thickness direction which is a cross sectional position of 45 to 55% with respect to the thickness, and when the crystal orientation is analyzed, the area ratio of Cube orientation {001} <100> is 5% or more, the area ratio of Brass orientation {110} <112> is 40% or less, and the area ratio of Copper orientation {112} <111> is 20% or less. According to this disclosure, by controlling the crystal orientation inside the copper alloy plate in this way, it is possible to obtain sufficient bending workability for notch bending.

[0005] Further, Patent Document 2 (WO2012/029717) discloses a copper alloy sheet material containing 1.0 to 5.0 mass% of Ti and the rest consisting of copper and inevitable impurities, wherein in the crystal orientation analysis by EBSD measurement, the copper alloy sheet material is characterized in that the area ratio of the Cube orientation {001} <100> is 5 to 50%. According to the disclosure, there is a correlation between the Cube orientation accumulation ratio and the bending workability, and by controlling this, a copper alloy sheet material having excellent bending workability and excellent strength can be obtained.

[0006] Further, Patent Document 3 (JP2015-190044A) discloses that, at the stage before finish cold rolling, by controlling the ratio of the maximum side average crystal grain size / average grain size to be smaller than a certain level, and by reducing the number density of coarse second phase particles, the level of the bending workability of the copper alloy sheet material can be improved and variations can be reduced. Moreover, Patent Document 4 (JP2004-052008A) discloses a titanium copper alloy material comprising Ti of 1.0 to 5.0 mass% and the rest consisting of copper and inevitable impurities, characterized in that the value of the ratio of (the deviation of crystal grain size) / (the average crystal grain size) is 0.60 or less, and the mechanical properties such as bending workability and stress relaxation property of the titanium copper alloy material are uniform and good.

Citation List**[Patent Document]**

[0007]

[Patent Document 1] JP2013-100586A
 [Patent Document 2] WO2012/029717
 [Patent Document 3] JP2015-190044A
 [Patent Document 4] JP2004-052008A

[Summary of Invention]

[Technical Problem to Be Solved]

[0008] Meanwhile, for the purpose of ensure clicking feeling during mounting, some of the materials for signal terminals are subjected to a beating process on both sides of the terminal in advance so as to reduce the plate thickness and then subjected to a bending process as before. At this time, the problem is that, since processing strain is introduced due to the beating process, when compared with the state in which the beating process is not conducted, the bending workability is impaired. For this reason, maintaining bending workability even when a beating process is conducted, is considered a problem. Although the inventions described in Patent Documents 1 to 4 have certain effects in improving the bending workability, in order to respond to the requirement of bending workability of titanium copper for electronic components to which beating process is applied, further improvement is desired.

[0009] Therefore, it is an object of present invention to improve bending workability of titanium copper for electronic components, and to provide a titanium copper for electronic components, which has excellent bending workability even when subjected to beating process, and to provide a method for manufacturing the same.

[Solution to Problem]

[0010] In order to solve the above technical problem, the inventors of the present invention conducted extensive research and discovered findings that, in order to improve the bending workability of titanium copper for electronic components to which beating process is applied, it is important to simultaneously control the coefficient of variation of crystal grain size when orientation difference of 5° or more is defined as a crystal grain boundary, and the area ratio of Cube orientation {001} <100>.

[0011] Besides, the inventors also discovered finding that, to realize the control described above, when manufacturing a titanium copper by hot rolling an ingot of titanium copper, followed by a step of cold rolling and a final solution heat treatment, it is necessary to make the minimum working ratio per pass and the total working degree in the step of cold rolling within a certain range, while setting the rate of temperature rise and the heating temperature in the step of final solution heat treatment in a certain range.

[0012] The present invention is accomplished based on the above findings.

[0013] Accordingly, the present invention is described as below:

(1) A titanium copper, comprising 2.0 to 4.5 mass% of Ti, and at least one element in total selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities,

wherein in a crystal orientation analysis by EBSD measurement on the rolled surface, when an orientation difference of 5° or more is defined as a crystal grain boundary, a coefficient of variation of crystal grain size is 45% or less, and an area ratio of Cube orientation {001} <100> is 5% or less.

(2) The titanium copper according to (1), wherein when a W bending test was performed in the Badway direction at $r/t = 1.0$ in accordance with JIS-H 3130 (2012) after a cold rolling with a working ratio of 10%, the average roughness Ra of the outer peripheral surface of the bent portion is 1.0 μm or less.

(3) The titanium copper according to (1) or (2), wherein in the crystal orientation analysis by EBSD measurement on the rolled surface, when an orientation difference of 5° or more is defined as a crystal grain boundary, an average crystal grain size is 2 to 30 μm .

(4) The titanium copper according to any one of (1) to (3), wherein when a tensile test is performed according to JIS-Z 2241 (2011), a 0.2% yield strength in a direction parallel to the rolling direction is 800 MPa or more.

(5) An electronic component, comprising the titanium copper according to any one of (1) to (4).

(6) A method for manufacturing the titanium copper according to any one of (1) to (4), the method comprising:

a step of hot rolling an ingot of titanium copper, the ingot comprising 2.0 to 4.5 mass% of Ti, and at least one element selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities;

a step of cold rolling; and subsequently

a step of final solution heat treatment;

wherein in the step of cold rolling before the step of final solution heat treatment, the minimum working ratio per pass is 10 to 30%, and when the total working degree η is indicated as $\eta = \ln \{(\text{thickness before cold rolling}) / (\text{thickness after cold rolling})\}$, the η is 1.0 or more and less than 3.0; and wherein in the step of final solution heat treatment, when the addition amount (mass%) of Ti is X, the heating temperature (°C) is $(52 \times X + 610)$ to $(52 \times X + 680)$, and the rate of temperature rise at 400 °C or higher is 20 to 30 °C/s.

[Effect of Invention]

[0014] According to the present invention, bending workability of titanium copper for electronic components can be improved, and a titanium copper for electronic components, which has excellent bending workability even when subjected to beating process, as well as a method for manufacturing the same, can be provided.

[Description of Embodiments]

(Ti Concentration)

[0015] In the titanium copper according to the present invention, the Ti concentration is set to 2.0 to 4.5 mass%. In the titanium copper, Ti is solidified in the Cu matrix by solution treatment, and fine precipitates are dispersed in the alloy by aging treatment, thereby increasing strength and conductivity.

[0016] When the Ti concentration is less than 2.0 mass%, precipitation of precipitates becomes insufficient and desired strength can not be obtained. When the Ti concentration exceeds 4.5% by mass, the processability is deteriorated, and the material is easily broken during rolling. Considering the balance of strength and workability, the preferable Ti concentration is 2.5 to 3.5 mass%.

(Third Element(s))

[0017] In the titanium copper according to the present invention, one or more third element(s) selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg and Si can be contained, and thereby the strength can be further improved. However, when the total concentration of the third element(s) exceeds 0.5% by mass, the processability is deteriorated, and the material is easily broken during rolling. Therefore, these third elements can be contained in a total amount of 0 to 0.5 mass%. In view of the balance between strength and workability, it is preferable to contain one or more of the above elements in a total amount of 0.1 to 0.4 mass%. Further, for each additional element, Zr, P, B, V, Mg and Si in an amount of 0.01 to 0.15 mass%, Fe, Co, Ni, Cr, Mo, Nb and Mn in an amount of 0.01 to 0.3 mass%, and Zn in an amount of 0.1 to 0.5 mass%, may be contained.

(Coefficient of Variation of Crystal Grain Size)

[0018] The titanium copper according to the present invention is characterized in that the relative variation in crystal grain size is small. This variation is evaluated using a coefficient of variation calculated from the average crystal grain size and standard deviation, particularly, from the formula: standard deviation / average crystal grain size $\times$ 100. The value of the coefficient of variation is set to 45% or less.

[0019] If the coefficient of variation of crystal grain size is within the above range, variations in crystal grain size can be suppressed, and dislocation becomes uniform, and stress at the time of bending is dispersed, and improvement in bending workability can be expected. From this viewpoint, the coefficient of variation of crystal grain size is preferably 43% or less, more preferably 41% or less, still more preferably 39% or less.

[0020] Besides, the average crystal grain size and the standard deviation are obtained by analyzing crystal orientation with the EBSD (Electron Back Scatter Diffraction) measurement on the rolled surface, using analysis software attached to EBSD (e.g. OIM Analysis provided by TSL Solutions Co., Ltd.), wherein the average crystal grain size and the standard deviation are calculated when an orientation difference of 5° or more is defined as a grain boundary.

[0021] In the present invention, the following conditions are adopted as measurement conditions in the EBSD measurement.

(A) SEM conditions

[0022]

- Beam condition: acceleration voltage 15 kV, irradiation current amount 5×10^{-8} A

- Working distance: 25 mm
- Observation visual field: $200\ \mu\text{m} \times 200\ \mu\text{m}$
- Observation surface: rolled surface
- Pretreatment of the observation surface: electrolytic polishing in a solution of phosphoric acid 67% + sulfuric acid 10% + water under a condition of $15\ \text{V} \times 60\ \text{seconds}$ to expose the structure

(B) EBSD conditions

[0023]

- Measurement program: OIM Data Collection
- Data analysis program: OIM Analysis (Ver.5.3)
- Step width: $0.5\ \mu\text{m}$

(Area Ratio of Cube Orientation)

[0024] In the titanium copper according to the present invention, the area ratio of the Cube orientation $\{001\} \langle 100 \rangle$ is controlled to 5% or less. If the area ratio of the Cube orientation is 5% or less, in combination with the coefficient of variation of the crystal grain size described above, the bending workability of the titanium copper according to the present invention can be improved.

[0025] The reason for improving the bending workability of titanium copper is not clear, but it is presumed as follows. That is, when bending is applied, plastic deformation normally occurs, and strain accumulates in crystal grains. However, the Cube orientation is hard to be plastically deformed, and strain is hard to be introduced by bending processing. When the proportion of Cube orientation increases, the accumulation of strain becomes unbalanced and cracks are generated due to the locally accumulated strain. On the contrary, when the proportion of Cube orientation is small, the accumulation of strain becomes uniform and bending workability is improved. Furthermore, by reducing crystal grain size, the amount of strain accumulated in each crystal grain size is reduced, and the bendability is improved.

[0026] Herein, the Cube orientation refers to a state in which the (001) plane is oriented in the normal direction (ND) of the rolled surface and the (100) plane is in the rolling direction (RD) in crystal orientation analysis by EBSD measurement on the rolled surface. It is indicated by an index of $\{001\} \langle 100 \rangle$.

(Bending Workability)

[0027] The titanium copper according to the present invention can have excellent bending workability. In one embodiment of the titanium copper according to the present invention, when a cold rolling with a working ratio of 10%, which simulates a beating process, is conducted, and subsequently a W bending test was performed in the Badway direction at $r/t = 1.0$ in accordance with JIS-H 3130 (2012) after the cold rolling, the average roughness R_a of the outer peripheral surface of the bent portion is $1.0\ \mu\text{m}$ or less. The average roughness R_a is calculated according to JIS-B 0601 (2013). The fact that the average roughness of the bent portion is small even after the bending means that harmful cracks which may cause breakage are difficult to occur in the bent portion. Generally, the average roughness R_a of the surface of the titanium copper according to the present invention before the bending test is $0.2\ \mu\text{m}$ or less.

[0028] The working ratio, which simulates a beating process, is based on the following equation. In the equation, T_0 is the thickness of the ingot before the cold rolling and T is the thickness of the ingot at the end of the cold rolling.

$$\text{Working Ratio (\%)} = \{(T_0 - T) / T_0\} \times 100$$

(Average Crystal Grain Size)

[0029] From the viewpoint of improving strength, bending workability and fatigue characteristics in a well-balanced manner, in one embodiment of titanium copper according to the present invention, it is preferable to control the average crystal grain size in the rolled surface within the range of 2 to $30\ \mu\text{m}$, more preferably in the range of 2 to $15\ \mu\text{m}$, and still more preferably in the range of 2 to $10\ \mu\text{m}$.

[0030] As with the average crystal grain size used to calculate the coefficient of variation of crystal grain size described above, the average crystal grain size means the average crystal grain size obtained by analyzing the crystal orientation in the EBSD (Electron Back Scatter Diffraction) measurement on the rolled surface, using analysis software attached to EBSD (e.g. OIM Analysis provided by TSL Solutions Co., Ltd.), wherein the average crystal grain size is calculated when an orientation difference of 5° or more is defined as a grain boundary.

(0.2% Yield Strength)

[0031] In some embodiments of the titanium copper according to the present invention, 0.2% yield strength in a direction parallel to the rolling direction may be 800 MPa or more. The 0.2% yield strength of titanium copper according to the present invention may be 850 MPa or more in a preferred embodiment, 900 MPa or more in a further preferred embodiment, and 950 MPa or more in a further preferred embodiment.

[0032] The upper limit of the 0.2% yield strength is not particularly restricted from the viewpoint of the strength intended by the present invention, but since it is troublesome and expensive, the 0.2% yield strength of titanium copper according to the present invention is generally 1300 MPa or less, typically 1200 MPa or less, more typically 1100 MPa or less.

[0033] In the present invention, the 0.2% yield strength in the direction parallel to the rolling direction is measured in accordance with JIS-Z 2241 (2011) (method for metal material tensile test).

(Thickness of Titanium Copper)

[0034] In one embodiment of titanium copper according to the present invention, the thickness can be 1.0 mm or less. In a typical embodiment, the thickness can be 0.02 to 0.8 mm, and in an more typical embodiment, the thickness can be 0.05 to 0.5 mm.

(Application)

[0035] Titanium copper according to the present invention can be processed into various copper elongation products such as plates, strips, pipes, rods and wires. The titanium copper according to the present invention is preferably used as a conductive material or a spring material in electronic components such as a switch, a connector, an autofocus camera module, a jack, a terminal (in particular, a battery terminal), a relay and the like, although its application is not limited. These electronic components can be used, for example, as in-vehicle parts or parts for electrical and electronic equipment.

(Manufacturing Method)

[0036] Hereinafter, preferable production examples of the titanium copper according to the present invention will be sequentially described for each step.

<Preparation of Ingot>

[0037] Preparation of ingot by melting and casting is basically carried out in vacuum or in an inert gas atmosphere. If undissolved residues of the added element(s) is present during dissolution, it does not work effectively for improving the strength. Therefore, in order to eliminate undissolved residues, for third elements having a high melting point such as Fe or Cr, after add the element, it is necessary to sufficiently stir it, and to maintain a certain period of time. On the other hand, since Ti is relatively soluble in Cu, it may be added after dissolution of the third element(s). Therefore, it is desirable to at first add one or more elements selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg and Si in total of 0 to 0.5 mass%, and then add Ti to a concentration of 2.0 to 4.5 mass%, so as to produce an ingot.

<Homogenization Annealing and Hot Rolling>

[0038] Since solidifying segregation and crystallization that occurred at the time of preparation of ingot are coarse, it is desirable to solidify them in the matrix to make them smaller, and more desirable to eliminate them as much as possible by homogenization annealing. This is because it is effective in preventing bending cracks. Specifically, after the ingot preparation process, it is preferable to perform homogenization annealing by heating to 900 to 970 °C and keeping for 3 to 24 hours, and then to perform hot rolling. In order to prevent liquid metal brittleness, it is preferable to set the temperature to 960 °C or less before and during the hot rolling, and to set the temperature to 900 °C or more during passes from the original thickness to the total reduction rate of 90%.

<Cold Rolling and Annealing>

[0039] After the hot rolling, cold rolling is performed. The working ratio of the cold rolling is typically 30% or more.

[0040] Subsequently, annealing can then be carried out. Here, the annealing conditions are typically 900 °C. and 1 to 5 minutes. The cold rolling and the annealing can be repeated as necessary.

<First Solution Heat Treatment

[0041] After appropriately repeating the cold rolling and the annealing, it is preferable to perform a first solution heat treatment. Here, the reason for preliminarily performing solution heat treatment is to reduce the burden on the final solution treatment. That is, in the final solution heat treatment, since the second phase particles are already solutionized, heat treatment for solid solution of the second phase particles is not necessary, and it is only necessary to maintain this state and further cause recrystallization, so that a slight heat treatment is sufficient. Specifically, the first solution heat treatment may be performed at a heating temperature of 850 to 900 °C for 2 to 10 minutes. It is also preferable to make the heating rate and the cooling rate at that time as high as possible and to prevent precipitation of the second phase particles during this process. Note that the first solution heat treatment may not be performed.

<Intermediate rolling>

[0042] The area ratio of the Cube orientation and the coefficient of variation of the crystal grain size are greatly affected by recrystallization in the final solution heat treatment. Since the driving force of recrystallization is the strain introduced by intermediate rolling which is the previous process, it becomes important to control the minimum working ratio per pass and the total working degree. Here, it is necessary to set the minimum working ratio per pass to 10 to 30%, and when the total working degree η is indicated as $\eta = \ln \{(\text{thickness before cold rolling}) / (\text{thickness after cold rolling})\}$, it is necessary to set the η to 1.0 or more and less than 3.0.

[0043] When the minimum working ratio per pass is less than 10%, it becomes difficult to control the area ratio of the Cube orientation of finally obtained titanium copper to 5% or less, whereas if the minimum working ratio per pass exceeds 30%, the material breaks and the production becomes difficult. From this viewpoint, the minimum working ratio per pass is preferably 13 to 27%, more preferably 16 to 24%.

[0044] Further, when the total working degree η is less than 1.0, it becomes difficult to control the coefficient of variation of the crystal grain size of finally obtained titanium copper to 45% or less, whereas when the total processing degree η is 3.0 or more, it also becomes difficult to control the coefficient of variation of the crystal grain size of finally obtained titanium copper to 45% or less. From this viewpoint, the total working degree η is preferably 1.3 to 2.7, more preferably 1.6 to 2.4.

[0045] The working ratio per pass can be obtained from the following equation. In the equation, T_0 is the thickness of the ingot before the cold rolling and T is the thickness of the ingot at the end of the cold rolling.

$$\text{Working Ratio (\%)} = \{(T_0 - T) / T_0\} \times 100$$

<Final Solution Heat Treatment>

[0046] In the final solution heat treatment, it is desirable to completely dissolve the precipitates, but when heated to a high temperature until precipitates are completely eliminated, the crystal grains tend to coarsen, so the heating temperature is set close to the solid solubility limit of the second phase particle composition. Specifically, when the addition amount (mass%) of Ti is X , the heating temperature (°C) is set to $(52 \times X + 610)$ to $(52 \times X + 680)$. When the heating temperature is lower than $52 \times X + 610$, recrystallization becomes insufficient, and when the heating temperature exceeds $52 \times X + 680$, the crystal grain size becomes coarse, and the bending workability of finally obtained titanium copper is remarkably deteriorated. Here, it is necessary to control the rate of temperature rise at 400 °C or higher to 20 to 30 °C/s. In the temperature range of 400 °C or higher, when the rate of temperature rise is less than 20 °C/s, precipitation occurs during the temperature rising process because the heating time is prolonged, and when the rate of temperature rise exceeds 30 °C/s, As the time is shortened, it becomes an unstable heat treatment, and as a result, it becomes difficult to control the coefficient of variation of the crystal grain size of finally obtained titanium copper to 45% or less.

[0047] In addition, shorter heating time in the final solution heat treatment can suppress coarsening of crystal grains. The heating time can be, for example, 30 seconds to 10 minutes, and typically 1 minute to 8 minutes. During this period, even if second phase particles are generated, as long as they are finely and uniformly dispersed, they are almost harmless to strength and bending workability. However, coarse particles tend to grow further in the final aging treatment, so if second phase particles are generated during this period, they should be made as few as possible and should be made as small as possible.

<Final Cold Rolling>

[0048] The final solution heat treatment is followed by the final cold rolling. Although the strength can be increased by the final cold rolling, in order to obtain bending workability as intended in the present invention, it is desirable set to the

reduction ratio to 5 to 50%, preferably to 20 to 40%.

<Aging treatment>

[0049] The final cold rolling is followed by aging treatment. It is preferable to heat at a material temperature of 300 to 500 °C for 1 to 50 hours, more preferably at a material temperature of 350 to 450 °C for 10 to 30 hours. The aging treatment is preferably performed in an inert atmosphere such as Ar, N₂, H₂ or the like in order to suppress the generation of the oxide film.

[0050] Summarizing the above, in one embodiment of the method for manufacturing titanium copper according to the present invention, the method comprises:

a step of preparing an ingot of titanium copper, the ingot comprising 2.0 to 4.5 mass% of Ti, and at least one element selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities;

a step of hot rolling the ingot;

a step of cold rolling, wherein the minimum working ratio per pass is 10 to 30%, and when the total working degree η is indicated as $\eta = \ln \{(\text{thickness before cold rolling}) / (\text{thickness after cold rolling})\}$, the η is 1.0 or more and less than 3.0; and

a step of final solution heat treatment, wherein when the addition amount (mass%) of Ti is X, the heating temperature (°C) is $(52 \times X + 610)$ to $(52 \times X + 680)$, and the rate of temperature rise at 400 °C or higher is 20 to 30 °C/s.

[0051] Those skilled in the art will appreciate that steps such as grinding, polishing, shot-blast acid washing and the like for removing oxide scales on the surface can be appropriately performed between the above steps.

[Examples]

[0052] Hereinafter, the present invention will be specifically described using examples and comparative examples. However, The descriptions of the following examples and comparative examples are merely specific examples for facilitating understanding of the technical contents of the present invention and the technical scope of the present invention is not limited by these specific examples.

[0053] Alloys containing the alloy components shown in Table 1 and the rest consisting of copper and inevitable impurities were used as an experimental materials and effects of the alloy components, the production conditions for cold rolling and subsequent final solution heat treatment on the 0.2% yield strength, the coefficient of variation of crystal grain size, the area ratio of Cube orientation and the bending workability after rolling were investigated.

[0054] First, 2.5 kg of electrolytic copper was dissolved in a vacuum melting furnace, and third element(s) was added at the mixing ratio shown in Table 1, and then Ti of the compounding ratio shown in the same table was added. After carefully considering the retention time after addition so that there is no residue of added elements, these were injected into a mold in Ar atmosphere to produce ingots of about 2 kg each.

[0055] After homogenizing annealing to the ingot at 950 °C for 3 hours, hot rolling was performed at 900 to 950 °C to obtain a hot rolled sheet having a thickness of 15 mm. After descaling by surface milling, cold rolling and annealing were repeated to obtain strip thicknesses (0.3 to 3.3 mm), and a first solution heat treatment was performed on the stripes. The conditions of the first solution heat treatment were heating at 850 °C for 10 minutes and then water cooling. Subsequently, intermediate cold rolling was carried out under the conditions shown in Table 1, then inserted into an annealing furnace which is capable of rapid heating, and the final solution treatment was performed, followed by water cooling. The heating conditions at this time were set as shown in Table 1. Then, after descaling by acid washing, final cold rolling with a reduction ratio of 25% was performed to obtain a plate thickness of 0.1 mm and finally subjected to aging treatment at 400 °C $\times$ 20 hours to obtain test pieces of the Examples and Comparative Examples Respectively.

[0056] The following tests were conducted on the prepared test pieces.
(0.2% yield strength)

JIS 13B test piece was prepared and the 0.2% yield strength in the direction parallel to the rolling direction was measured using a tensile tester according to the above measuring method.

(Average crystal grain size)

[0057] After polishing the plate surface (rolled surface) of each test piece and etching it, in the analysis of crystal orientation by EBSD (Electron Back Scatter Diffraction) measurement, using analysis software attached to EBSD (eg, OIM Analysis provided by TSL Solutions Co., Ltd.), the average crystal grain size in the case where the orientation difference of 5° or more was defined as a grain boundary was measured.

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(Coefficient of variation of crystal grain size)

[0058] After polishing the plate surface (rolled surface) of each test piece and etching it, in the analysis of crystal orientation by EBSD (Electron Back Scatter Diffraction) measurement, using analysis software attached to EBSD (eg, OIM Analysis provided by TSL Solutions Co., Ltd.), the average crystal grain size and the standard deviation in the case where the orientation difference of 5° or more was defined as a grain boundary was measured, and the value of standard deviation / average crystal grain size $\times$ 100 was taken as the coefficient of variation of crystal grain size.

(Area ratio of Cube orientation (%))

[0059] After polishing the plate surface (rolled surface) of each test piece and etching it, in the analysis of crystal orientation by EBSD (Electron Back Scatter Diffraction) measurement, the area ratio (%) of the Cube orientation was measured. When the deviation angle from the Cube orientation was within 15°, it is regarded as in Cube orientation.

(Bendability after rolling)

[0060] A cold rolling with a working ratio of 10%, which simulates a beating process, was conducted, and subsequently a W bending test was performed in the Badway direction at $r/t = 1.0$ in accordance with JIS-H 3130 (2012) after the cold rolling. The outer peripheral surface of the bent portion of this test piece was observed. For the observation method, the outer peripheral surface of the bent portion was photographed using a confocal microscope HD100 manufactured by Lasertec Corporation, and the average roughness Ra (according to JIS-B 0601: 2013) was measured using the attached software and compared. When the surface of the sample before bending was observed with a confocal microscope, irregularities were not confirmed, and the average roughness Ra was 0.2 μm or less in each case. A case where the surface average roughness Ra after bending was 1.0 μm or less was evaluated as "OK" and a case where Ra was more than 1.0 μm was evaluated as "NG".

[Table 1]

	Conditions for production						Final characteristics				
	Component (mass%)		Cold rolling before final solution heat treatment		Final solution heat treatment						
Ti	Third element	minimum working ratio per pass(%)	total working degree (η)	rate of temperature rise at 400 °C or higher (°C/s)	heating temperature (°C)	0.2% yield strength (MPa)	average crystal grain size (μm)	coefficient of variation of crystal grain size (%)	Area ratio of Cube orientation (%)	bendability after rolling	
Example 1	3.2	0.2Fe	20	2.3	25	800	966	5	38	2.4	OK
Example 2	3.2	0.2Fe	12	2.3	25	800	956	6	39	4.5	OK
Example 3	3.2	0.2Fe	28	2.3	25	800	954	5	35	0.8	OK
Example 4	3.2	0.2Fe	20	1.1	25	800	961	6	43	2.1	OK
Example 5	3.2	0.2Fe	20	2.9	25	800	960	6	33	2.2	OK
Example 6	3.2	0.2Fe	20	2.3	22	800	945	5	42	2.6	OK
Example 7	3.2	0.2Fe	20	2.3	28	800	944	6	36	2.5	OK
Example 8	3.2	0.2Fe	20	2.3	25	750	956	3	35	2.4	OK
Example 9	3.2	0.2Fe	20	2.3	25	840	930	15	39	2.0	OK
Example 10	3.2	-	20	2.3	25	800	925	20	35	3.2	OK
Example 11	2.0	-	20	2.3	25	750	833	25	40	3.7	OK
Example 12	4.5	-	20	2.3	25	880	1097	20	35	2.7	OK
Example 13	3.2	0.2Mo- 0.05Mg	25	2.3	25	820	963	8	36	2.9	OK
Example 14	3.2	0.2Ni- 0.05B	15	1.5	25	790	945	7	42	3.8	OK
Example 15	3.2	0.05Zr- 0.05P	20	2	25	810	959	13	40	3.4	OK
Example 16	3.2	0.4Zn- 0.05V	25	1.8	25	800	952	16	42	1.4	OK

(continued)

	Conditions for production						Final characteristics				
	Component (mass%)		Cold rolling before final solution heat treatment		Final solution heat treatment		0.2% yield strength (MPa)	average crystal grain size (μm)	coefficient of variation of crystal grain size (%)	Area ratio of Cube orientation (%)	bendability after rolling
			minimum working ratio per pass(%)	total working degree (η)	rate of temperature rise at 400 °C or higher (°C/s)	heating temperature (°C)					
Example 17	3.2	Third element	15	2.6	25	820	958	14	35	3.1	OK
Example 18	3.2	0.2Cr- 0.1Mn- 0.05Nb	25	2	25	830	948	10	38	2.2	OK
Comparative Example 1	3.2	0.2Fe	7	2.3	25	800	956	7	42	7.3	NG
Comparative Example 2	3.2	0.2Fe	(35)	Not manufacturable			-	-	-	-	-
Comparative Example 3	3.2	0.2Fe	20	0.8	25	800	943	6	51	2.6	NG
Comparative Example 4	3.2	0.2Fe	20	3.2	25	800	952	5	48	2.9	NG
Comparative Example 5	3.2	0.2Fe	20	2.3	16	800	965	5	52	3.1	NG
Comparative Example 6	3.2	0.2Fe	20	2.3	34	800	964	5	50	2.4	NG
Comparative Example 7	3.2	0.2Fe	20	2.3	25	750	975	Unrecrystallized	-	-	NG
Comparative Example 8	3.2	0.2Fe	20	2.3	25	850	915	35	53	2.4	NG
Comparative Example 9	3.2	0.3Fe- 0.3Ni	Not manufacturable				-	-	-	-	-

(continued)

	Conditions for production					Final characteristics				
	Cold rolling before final solution heat treatment		Final solution heat treatment			0.2% yield strength (MPa)	average crystal grain size (μm)	coefficient of variation of crystal grain size (%)	Area ratio of Cube orientation (%)	bendability after rolling
	Component (mass%)	Third element	minimum working ratio per pass(%)	total working degree (η)	rate of temperature rise at 400 °C or higher (°C/s)					
Comparative Example 10	1.5	0.2Fe	20	2.3	25	753	5	38	6.7	NG
Comparative Example 11	5.0	0.2Fe	Not manufacturable			-	-	-	-	-
Comparative Example 12	3.2	-	8	0.9	25		18	43	6.6	NG

(Discussions)

[0061] In Examples 1 to 18, the coefficient of variation of the crystal grain size is 45% or less and the area ratio of the Cube orientation is 5% or less, so that the bending workability is excellent. Further, the average crystal grain size was 2 to 30 μm , and the 0.2% yield strength was 800 MPa or more.

[0062] On the other hand, in Comparative Example 1, since the minimum working ratio per pass was too low, the area ratio of the Cube orientation was outside the range of the present invention, and the bending workability was inferior to the Examples.

[0063] In Comparative Example 2, the minimum working ratio per pass was too high, and as a result the material broke and it was impossible to continue production.

[0064] Since the total working degree of Comparative Example 3 and 4 was outside the range of the present invention, the coefficient of variation of the crystal grain size was outside the range of the present invention. Therefore, the bending workability was inferior to the Examples.

[0065] Since the rate of temperature rise in Comparative Example 5 and 6 at 400 °C or higher was outside the range of the present invention, the coefficient of variation of the crystal grain size was outside the range of the present invention. Therefore, the bending workability was inferior to the Examples.

[0066] Since the heating temperature in Comparative Example 7 was too low, recrystallization was insufficient, and titanium copper intended for the present invention could not be produced.

[0067] Since the heating temperature in Comparative Example 8 was too high, the coefficient of variation of the crystal grain size exceeded the upper limit of the present invention. Therefore, the bending workability was inferior to the Examples.

[0068] Since the third element(s) added to Comparative Example 9 was too much, the material cracked during rolling, and titanium copper intended for the present invention could not be produced.

[0069] Since the amount of Ti added to Comparative Example 10 was too small, the area ratio of the Cube orientation exceeded the upper limit of the present invention. Therefore, the bending workability was inferior to the Examples.

[0070] Since the amount of Ti added to Comparative Example 11 was too large, the material cracked during rolling, and titanium copper intended for the present invention could not be produced.

[0071] Comparative Example 12 was produced in accordance with the invention according to Patent Document 4 described above. In Comparative Example 12, the minimum working ratio per pass is low and the total working degree is also low. Moreover, the heating temperature is higher than the range of the present invention. As a result, the area ratio of the Cube orientation exceeded the upper limit of the present invention, and the bending workability was inferior to the Examples.

Claims

1. A titanium copper, comprising 2.0 to 4.5 mass% of Ti, and at least one element selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities, wherein in a crystal orientation analysis by EBSD measurement on the rolled surface, when an orientation difference of 5° or more is defined as a crystal grain boundary, a coefficient of variation of crystal grain size is 45% or less, and an area ratio of Cube orientation {001} <100> is 5% or less.
2. The titanium copper according to claim 1, wherein when a W bending test was performed in the Badway direction at $r/t = 1.0$ in accordance with JIS-H 3130 (2012) after a cold rolling with a working ratio of 10%, the average roughness Ra of the outer peripheral surface of the bent portion is 1.0 μm or less.
3. The titanium copper according to claim 1 or 2, wherein in the crystal orientation analysis by EBSD measurement on the rolled surface, when an orientation difference of 5° or more is defined as a crystal grain boundary, an average crystal grain size is 2 to 30 μm .
4. The titanium copper according to any one of claims 1 to 3, wherein when a tensile test is performed according to JIS-Z 2241 (2011), a 0.2% yield strength in a direction parallel to the rolling direction is 800 MPa or more.
5. An electronic component, comprising the titanium copper according to any one of claims 1 to 4.
6. A method for manufacturing the titanium copper according to any one of claims 1 to 4, the method comprising:

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a step of hot rolling an ingot of titanium copper, the ingot comprising 2.0 to 4.5 mass% of Ti, and at least one element selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si in total of 0 to 0.5 mass% as a third element(s), and the rest consisting of copper and inevitable impurities;

a step of cold rolling; and subsequently

a step of final solution heat treatment;

wherein in the step of cold rolling before the step of final solution heat treatment, the minimum working ratio per pass is 10 to 30%, and when the total working degree η is indicated as $\eta = \ln \{(\text{thickness before cold rolling}) / (\text{thickness after cold rolling})\}$, the η is 1.0 or more and less than 3.0; and

wherein in the step of final solution heat treatment, when the addition amount (mass%) of Ti is X, the heating temperature (°C) is $(52 \times X + 610)$ to $(52 \times X + 680)$, and the rate of temperature rise at 400 °C or higher is 20 to 30 °C/s.

REFERENCES CITED IN THE DESCRIPTION

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