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(71) Applicant: **JX Nippon Mining & Metals Corp.**
Chiyoda-ku
Tokyo 1008164 (JP)

(72) Inventor: **HORIE, Hiroyasu**
Hitachi-shi, Ibaraki 3170056 (JP)

(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) TITANIUM COPPER, METHOD FOR PRODUCING TITANIUM COPPER AND ELECTRONIC COMPONENT

(57) Provided is titanium copper having improved stress relaxation resistance, a method for producing the titanium copper, and an electronic component using the titanium copper. A titanium copper which contains from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, wherein a pole density of <111> is from 2.5 to 4.5, and a pole density of <001> is higher than that of <101>, in an inverse pole figure in a rolling direction.

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Description

TECHNICAL FIELD

[0001] The present invention relates to titanium copper, a method for producing titanium copper, and an electronic component. For example, the present invention relates to titanium copper, a method for producing the titanium copper and an electronic component using the titanium copper, which are suitable for use in electronic components such as connectors, battery terminals, jacks, relays, switches, autofocus camera modules, and lead frames.

BACKGROUND ART

[0002] Recently, progressing miniaturization of electronic components such as lead frames and connectors used in electric/electronic devices and on-board components is bringing about remarkable tendencies to narrow a pitch and reduce a height of a copper alloy member forming an electronic component. A smaller connector has a narrower pin width, resulting in a smaller folded shape, so that the copper alloy member to be used is required to have high strength in order to obtain required spring properties. In this respect, a copper alloy containing titanium (hereinafter referred to as "titanium copper") has a relatively high strength and the best stress relaxation resistance among copper alloys. Therefore, the titanium copper has been traditionally used as a signal system terminal member.

[0003] The titanium copper is an age-hardening copper alloy, which has a good balance between strength and bending workability, and additionally exhibits particularly improved characteristics among various copper alloys in terms of stress relaxation resistance. Therefore, developments have been made to improve properties such as strength and bending workability while maintaining the stress relaxation resistance of the titanium copper.

[0004] Japanese Patent Application Publication No. 2014-185370 A (Patent Document 1) describes a Cu-Ti-based copper alloy sheet having improved bending workability while maintaining high strength and having improved fatigue resistance while maintaining good stress relaxation resistance, wherein the copper alloy has a composition of 2.0 to 5.0% by mass of Ti, 0 to 1.5% by mass of Ni, 0 to 1.0% by mass of Co, 0 to 0.5% by mass of Fe, 0 to 1.2% by mass of Sn, 0 to 2.0% by mass of Zn, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Zr, 0 to 1.0% by mass of Al, 0 to 1.0% by mass of Si, 0 to 0.1% by mass of P, 0 to 0.05% by mass of B, 0 to 1.0% by mass of Cr, 0 to 1.0% by mass of Mn, and 0 to 1.0% by mass of V, the total content of Sn, Zn, Mg, Zr, Al, Si, P, B, Cr, Mn and V among these elements being 3.0% or less, the balance being Cu and inevitable impurities, wherein the copper alloy sheet has a metal structure in which a maximum width of grain boundary reaction type precipitates is 500 nm or less and a density of granular precipitates having a diameter of 100 nm or more is 10^5/mm^2 or less in a cross section perpendicular to a thickness direction.

[0005] Japanese Patent Application Publication No. 2010-126777 A (Patent Document 2) describes a copper alloy sheet having improved bending workability while maintaining high strength, wherein the copper alloy sheet has a composition of 1.2 to 5.0% by mass of Ti, the balance being Cu and inevitable impurities, wherein an average crystal grain size is from 5 to 25 μm, and a ratio (maximum crystal grain size - minimum crystal grain size) / average crystal grain size is 0.20 or less, in which the maximum crystal grain size is a maximum value of average values of the crystal grain sizes in the respective regions of a plurality of regions having the same shape and sizes, which are randomly selected on the sheet surface, the minimum crystal grain size is a minimum value among average values of crystal grain sizes in the respective regions, and the average crystal grain size is an average value of the average values of the crystal grains in the respective regions, and wherein the copper alloy sheet has a crystal orientation satisfying $I\{420\} / I_0\{420\} > 1.0$, in which the $I\{420\}$ is an X-ray diffraction intensity of a {420} crystal plane on a sheet surface of the copper alloy sheet, and the $I_0\{420\}$ is an X-ray diffraction intensity of a {420} crystal plane of pure copper standard powder.

[0006] Japanese Patent Application Publication No. 2008-308734 A (Patent Document 3) describes a copper alloy sheet material having improved bending workability and improved stress relaxation resistance, as well as improved spring back, wherein the copper alloy sheet has a composition of 1.0 to 5.0% by mass of Ti, the balance being Cu and inevitable impurities, and wherein the copper alloy sheet has a crystal orientation satisfying $I\{420\} / I_0\{420\} > 1.0$, and has an average crystal grain size of 10 to 60 μm.

[0007] Japanese Patent Application Publication No. H07-258803 A (Patent Document 4) describes a method for producing a high-strength copper alloy having improved strength and improved bending workability by adjusting production steps from a solutionizing treatment to a cold rolling step, wherein the method comprises subjecting to a copper alloy containing 0.01 to 4.0% of Ti, the balance being Cu and inevitable impurities (1) a first solutionizing treatment carried out under heat treatment conditions of a temperature of 800 °C or higher within 240 seconds and an average crystal grain size of not more than 20 μm; (2) a first cold rolling carried out at a working ratio of less than 80%; (3) a second solutionizing treatment carried out under heat treatment conditions of a temperature of 800 °C or higher within 240 seconds and an average grain size of from 1 to 20 μm or less; (4) a second cold rolling carried out at a working ratio of 50% or less; and (5) an aging treatment at a temperature of from 300 to 700 °C for 1 hour to less than 15 hours in this order.

CITATION LIST

Patent Literatures

[0008]

Patent Document 1: Japanese Patent Application Publication No. 2014-185370 A
Patent Document 2: Japanese Patent Application Publication No. 2010-126777 A
Patent Document 3: Japanese Patent Application Publication No. 2008-308734 A
Patent Document 4: Japanese Patent Application Publication No. H07-258803 A

SUMMARY OF INVENTION

Technical Problem

[0009] Recently, electronic devices are required to have higher reliability in addition to higher functionality, and electronic components used for the electronic devices are also required to have higher reliability. In particular, heat resistance is one of important indices, which requires a higher level than the prior art. Titanium copper is known to have relatively better stress relaxation resistance. However, the titanium copper alloys disclosed in Patent Documents 1 to 4 still cannot provide sufficient stress relaxation resistance, and so there is a need for further improvement of stress relaxation resistance.

[0010] In view of the above problems, the present disclosure provides titanium copper having improved stress relaxation resistance, a method for producing the titanium copper, and an electronic component using the titanium copper.

Solution to Problem

[0011] As a result of intensive studies to solve the above problems, the present inventor has found that a titanium copper having a certain relationship among pole densities of <111>, <101> and <001> in an inverse pole figure in a rolling direction (RD) has improved stress relaxation resistance.

[0012] In one aspect, a titanium copper according to an embodiment of the present invention contains from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, wherein a pole density of <111> is from 2.5 to 4.5, and a pole density of <001> is higher than that of <101>, in an inverse pole figure in a rolling direction.

[0013] In one aspect, a method for producing titanium copper according to an embodiment of the present invention comprises casting a titanium copper ingot containing from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, and subjecting the cast ingot to hot rolling; and then carrying out a cold rolling step and a subsequent final solutionizing treatment step, wherein the hot rolling step comprises treating the ingot such that a compressive strain per pass is from 0.05 to 0.15 and a strain rate of a final pass is from 15.0 to 25.0, and wherein the final solutionizing treatment step comprises carrying out a treatment at a heating temperature (°C) of from $52 \times X + 610$ to $52 \times X + 680$ in which X is an addition amount (% by mass) of Ti, for a residence time of from 50 to 200 seconds.

Advantageous Effects of Invention

[0014] According to the present invention, it is possible to provide titanium copper having improved stress relaxation resistance, a method for producing the titanium copper, and an electronic component using the titanium copper.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

FIG. 1 is a view for explaining a measurement principle of a stress relaxation rate.
FIG. 2 is a view for explaining a measurement principle of a stress relaxation rate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Ti Concentration)

[0016] Titanium copper according to an embodiment of the present invention has a Ti concentration of from 2.0 to 4.5% by mass. The titanium copper has increased strength and increased electrical conductivity by dissolution of Ti in a Cu matrix with a solutionizing treatment and by dispersion of fine precipitates in the alloy with an aging treatment.

[0017] If the Ti concentration is less than 2.0% by mass, deposition of precipitates is not sufficient and any desired strength cannot be obtained. If the Ti concentration is more than 4.5% by mass, workability is deteriorated and the material is easily cracked during rolling. In terms of a balance between strength and workability, a preferable Ti concentration is from 2.5 to 3.5% by mass.

(Third Element)

[0018] The titanium copper according to an embodiment of the present invention contains at least one of third elements selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si, whereby the strength can be further improved. However, if the total concentration of the third elements is more than 0.5% by mass, the workability is deteriorated and the material is easily cracked during rolling. Therefore, these third elements can be contained in a total amount of from 0 to 0.5% by mass, and in view of the balance between strength and workability, the titanium copper preferably contains one or more of the above elements in a total amount of from 0.1 to 0.4% by mass. For each additive element, the titanium copper contains from 0.01 to 0.15% by mass of each of Zr, P, B, V, Mg, and Si, and from 0.01 to 0. 3% by mass of each of Fe, Co, Ni, Cr, Mo, Nb and Mn, and from 0.1 to 0.5% by mass of Zn.

(Inverse Pole Figure in RD Direction)

[0019] The titanium copper according to an embodiment of the present invention is characterized that a pole density of <111> is controlled within a certain range in an inverse pole figure in a RD direction, and a relationship between pole densities of <101> and <001> is constant. More particularly, the pole density of <111> is from 2.5 to 4.5, and the pole density of <001> is higher than the pole density of <101>. If both of these conditions are satisfied, the stress relaxation resistance can be further improved.

[0020] Although the relationship between the inverse pole figure in the RD direction and the stress relaxation resistance is not clearly understood, the pole density of <111> lower than 2.5 or higher than 4.5 cannot improve the stress relaxation resistance. Similarly, the pole density of <001> lower than that of <101> cannot improve the stress relaxation resistance. Further, even if the pole density of <111> is from 2.5 to 4.5, the pole density of <001> lower than that of <101> cannot improve the stress relaxation resistance, or even if the pole density of <001> is higher than that of <101>, the pole density of <111> lower than 2.5 or higher than 4.5 cannot improve the stress relaxation resistance.

[0021] Although not limited to the following, the pole density of <111> is preferably from 2.7 to 4.3, and more preferably from 2.9 to 4.1. The pole density of <101> is typically from 0 to 2.5, and the pole density of <001> is typically from 0.5 to 3.5.

[0022] As used herein, the "inverse pole figure in RD direction" refers to a measurement result of the inverse pole figure in the RD direction in crystal orientation analysis in EBSD (Electron Back Scatter Diffraction) measurement on a rolled surface using an analysis software (for example, OIM Analysis available from TSL Solutions, Inc.) attached to the EBSD. The Inverse pole figures can be obtained for the ND direction, the RD direction, and the TD direction. However, in this embodiment, the inverse pole figure in the RD direction is used in view of a stress axis applied when evaluating the stress relaxation resistance. It should be noted that the pole density in a state where the crystal orientation is random is 1.

[0023] In this embodiment, the following conditions are adopted for EBSD measurement:

(a) SEM conditions

- Beam Conditions: an acceleration voltage of 15 kV and an irradiation current of 5 × 10^{-8} A;
- Work Distance: 25mm;
- Observation Field: 150 μm × 150 μm;
- Observation Surface: rolled surface;
- Pre-treatment of Observation Surface: The structure is allowed to appear by electropolishing in a solution of 67% phosphoric acid + 10% sulfuric acid + water under conditions of 15V for 60 seconds.

(b) EBSD conditions

- Measurement Program: OIM Data Collection;
- Data analysis Program: OIM Analysis (Ver. 5.3); and
- Step Width: 0.25 μm.

(Stress Relaxation Resistance)

[0024] The titanium copper according to an embodiment of the present invention can have improved stress relaxation resistance. In one Embodiment, it has a feature that a stress relaxation rate is 10% or less after maintaining the titanium copper at 300 °C for 10 hours.

(Average Crystal Grain Size)

[0025] In one embodiment of the titanium copper according to the present invention, it is preferable to control an average crystal grain size on the rolled surface to a range of from 2 to 30 μm, more preferably to a range of from 2 to 15 μm, and even more preferably a range of from 2 to 10 μm, from the viewpoint of improving the strength, bending workability and fatigue characteristics with a good balance.

[0026] The average crystal grain size refers to an average crystal grain size in a case where an orientation difference of 5° or more is regarded as a crystal grain boundary by a crystal orientation analysis in EBSD (Electron Back Scattering Diffraction) measurement on the rolled surface using an analysis software (e.g.,, OIM Analysis available from TSL Solutions) attached to the EBSD, as with the average crystal grain size used for calculating the coefficient of variation of the crystal grain size as described above.

(0.2% Yield Strength)

[0027] In one embodiment, the titanium copper according to the embodiment of the present invention can achieve a 0.2% yield strength of 800 MPa or more in a direction parallel to the rolling direction. The 0.2% yield strength of the titanium copper according to the present invention is 850 MPa or more in a preferred embodiment, 900 MPa or more in a more preferred embodiment, and 950 MPa or more in an even more preferred embodiment.

[0028] The upper limit value of the 0.2% yield strength is not particularly limited from the viewpoint of the intended strength of the present invention. However, in terms of labors and costs, the upper limit is typically 1200 MPa or less, and more typically 1100 MPa or less.

[0029] In the present invention, the 0.2% yield strength of titanium copper in the direction parallel to the rolling direction is measured in accordance with JIS-Z2241 (2011) (Metal Material Tensile Test Method).

(Thickness of Titanium Copper)

[0030] In one embodiment, the titanium copper according to the present invention can have a thickness of 1.0 mm or less, and in a typical embodiment, it can have a thickness of from 0.02 to 0.8 mm, and in a more typical embodiment, it can have a thickness of from 0.05 to 0.5 mm.

(Use)

[0031] The titanium copper according to the present invention can be processed into various copper products, such as plates, strips, tubes, bars and wires. The titanium copper according to the present invention can preferably be used as a conductive material or a spring material in electronic parts including, but not limited to, switches, connectors, autofocus camera modules, jacks, terminals (particularly battery terminals), and relays. These electronic components can be used, for example, as on-board components or components for electric/electronic devices.

(Production Method)

[0032] Hereinafter, the method for producing the titanium copper according to an embodiment of the present invention includes casting an titanium copper ingot containing from 2.0 to 4.5% by mass of Ti, a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, and subjecting the cast ingot to hot rolling, and then carrying out a cold rolling step and a subsequent final solutionizing treatment step. Hereinafter, a suitable production example of the titanium copper according to this embodiment is sequentially described for each step.

<Production of Ingot>

[0033] 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 un-melted during melting, it does not effectively act on improvement of strength. Therefore, in order to eliminate un-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, to Cu is added at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si so as to contain them in a total amount of from 0 to 0. 5% by mass and then added Ti so as to contain it in an amount of from 2.0 to 4.5% by mass to produce the ingot.

<Homogenized Annealing and Hot Rolling>

[0034] Since solidifying segregation and crystallized matters produced during the production of the ingot are coarse, it is desirable to dissolving them in the parent 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 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, and that a temperature is preferably 700 °C or more for a pass from an original thickness to an entire working ratio of 80%.

[0035] In the present embodiment, a compressive strain per pass is from 0.05 to 0.15, and a strain rate of a final pass is from 15.0 to 25.0/s, and in a preferred embodiment, from 18.0 to 22.0/s. This can allow the pole density of <111> and the relationship between the pole densities of <101> and <001> in the inverse pole figure in the RD direction to be controlled to the above ranges. The compressive strain per pass can be calculated by dividing a compressive strain η = ln {(cross-sectional area before hot rolling) / (cross-sectional area after hot rolling)} by the total number of passes in hot rolling. Further, the strain rate ε (/s) is calculated from the following equation (1):

[Equation 1]

$$\varepsilon = \frac{2\pi n}{60\sqrt{r'}} \cdot \sqrt{\frac{R}{H_0}} \cdot \ln\left(\frac{1}{1-r'}\right) \quad \cdots (1)$$

in which H_0 is a sheet thickness (mm) on an inlet side, n is a rotation speed (rpm) of a rolling roll, R is a radius (mm) of the rolling roll, and r' is a working ratio ((sheet thickness on inlet side) - (sheet thickness on outlet side / sheet thickness on inlet side).

<Cold Rolling and Annealing>

[0036] After the hot rolling, cold rolling is carried out. The working ratio of the cold rolling is typically 60% or more. The working ratio per pass can be obtained according to the following Equation (2), where T_0 is a thickness of the ingot before rolling by the pass and T is a thickness of the ingot at the end of rolling by the pass:

$$\text{Working Ratio (\%)} = \{(T_0 - T) / T_0\} \times 100 \qquad (2)$$

Annealing can be then carried out. The annealing is typically carried out at 900 °C for 1 to 5 minutes. The cold rolling and annealing can be repeated as needed.

<First Solutionizing Treatment

[0037] A first solutionizing treatment is preferably carried out after repeating the cold rolling and annealing as needed. Here, the reason why the solutionizing treatment is carried out in advance is to reduce burdens in a final solutionizing treatment. That is, in the final solutionizing treatment, it is not a heat treatment for dissolving second phase grains and solutionizing is already achieved, so it is sufficient to cause recrystallization while maintaining that state and thus to be a light heat treatment. More particularly, the first solutionizing treatment may be carried out at a heating temperature of from 850 to 900 °C for 2 to 10 minutes. In this case, it is preferable to increase the heating rate and the cooling rate as much as possible so that the second phase grains do not precipitate. It should be noted that the first solutionizing treatment may not be carried out.

<Intermediate Rolling>

[0038] Intermediate rolling is then carried out. The working ratio of the intermediate rolling is typically 60% or more.

<Final Solutionizing Treatment

[0039] In the final solution treatment, it is desirable to dissolve precipitates completely. However, if heating is carried out at an elevated temperature until the precipitates are completely eliminated, the crystal grains tends to coarsen. Therefore, the heating temperature is near a solid solution limit of the second phase grain composition. More particularly, the heating temperature (°C) is in a range of from $52 \times X + 610$ to $52 \times X + 680$ where X is an addition amount (% by mass) of Ti.

[0040] In a case where the heating temperature is lower than $52 \times X + 610$ °C, it causes non-recrystallization, and in a case where the heating temperature is higher than $52 \times X + 680$, the crystal grain size becomes coarse. In both cases, the strength of titanium copper finally obtained is decreased.

[0041] The pole density of <111> and the relationship between the pole densities of <101> and <001> in the inverse pole figure in the RD direction can be controlled by adjusting a heating time in the final solutionizing treatment. The heating time can be, for example, from 50 to 200 seconds, and typically from 90 to 180 seconds.

<Final Cold Rolling>

[0042] Final cold rolling is carried out following the final solutionizing treatment. The final cold rolling can increase the strength. In order to obtain good stress relaxation resistance, the working ratio is preferably from 5 to 50%, and more preferably from 20 to 40%.

<Aging Treatment>

[0043] An aging treatment is carried out following the final cold rolling. Preferably, it is carried out by heating at a material temperature of from 300 to 500 °C for 1 to 50 hours, and more preferably heating at a material temperature of from 350 to 450 °C for 10 to 30 hours. The aging treatment is preferably carried out in an inert atmosphere such as Ar, N_2 and H_2 in order to suppress generation of an oxide film.

[0044] In summary, the method for producing the titanium copper according to the embodiment of the present invention includes:

a step of casting a titanium copper ingot containing from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities;
a hot rolling step of treating the cast ingot such that a compressive strain per pass is from 0.05 to 0.15 and a strain rate of a final pass is from 15.0 to 25.0/s; and
a final solutionizing treatment of treating the ingot at a heating temperature (°C) in a range of from $52 \times X + 610$ to $52 \times X + 680$ for a retention time of from 20 to 200 seconds, in which X is an addition amount (% by mass) of Ti.

[0045] It will be appreciated by a person skilled in the art that steps such as grinding, polishing, and shot blast pickling for removing oxide scales on the surface may be carried out between the above steps.

EXAMPLES

[0046] 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.

[0047] Each alloy containing the alloy components as shown in Table 1, the balance being copper and inevitable impurities, was used as an experimental material to investigate effects of production conditions of the alloy components, hot rolling and final solutionizing treatment on the pole density of <111> and the relationship between the pole densities of <101> and <001> in the inverse pole figure in the RD direction, and on the stress relaxation resistance.

[0048] First, 2.5 kg of electrolytic copper was melted in a vacuum melting furnace, and each third element was added at each mixing ratio as shown in Table 1, and Ti was then added at each mixing ratio as shown in Table 1. After sufficient consideration was given to the retention time after the addition such that there was no un-melted residue of the added elements, these were injected into a mold in an Ar atmosphere to produce about 2 kg of each ingot.

[0049] The ingot was subjected to homogenized annealing at 950 °C for 5 hours, followed by hot rolling at 900 to 950 °C to obtain a hot rolled sheet having a thickness of 10 mm. After descaling by chamfering, cold rolling and annealing were repeated to obtain a raw strip thickness (1.5 mm), and a first solutionizing treatment was carried out for the raw strip. The first solutionizing treatment was carried out by heating at 850 °C for 8 minutes, and then cooling in water. The intermediate cold rolling was then carried out, followed by the final solution treatment, and followed by cooling in water. Then, after descaling by pickling, the final cold rolling was carried out at a working ratio of 25% to obtain a sheet thickness of 0.1 mm, and finally the aging treatment was carried out under conditions of 400 °C for 20 hours to prepare each sample for Examples and Comparative Examples.

[0050] The following evaluations were conducted for the produced samples:

(0.2% Yield Strength)

[0051] Each JIS 13B sample 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 measurement method as described above.

(Average Crystal Grain Size)

[0052] After a sheet surface (rolled surface) of each sample was polished and etched, each sample was measured for an average crystal grain size in the case where an orientation difference of 5° or more was regarded as a crystal grain boundary, by crystal orientation analysis in EBSD (Electron Back Scatter Diffraction) measurement (e.g., OSL Analysis available from TSL Solutions) using an analysis software attached to the EBSD.

(Inverse Pole Figure)

[0053] An inverse pole figure in the RD direction was measured by crystal orientation analysis in an EBSD (Electron Back Scatter Diffraction) measurement on a rolled surface using an analysis software attached to the EBSD (for example, OIM Analysis available from TSL Solutions), and pole densities of <111 >, <101 >, <001> were evaluated. A case where the pole density of <001> was higher than the pole density of <101> was determined to be "○", and a case where the pole density of <101> was less than or equal to the pole density of <001> was determined to be "x".

(Stress Relaxation Resistance)

[0054] The stress relaxation rate after maintaining each sample at 300 °C for 10 hours was measured. Each strip-shaped sample having a width of 10 mm and a length of 100 mm was collected such that a longitudinal direction of the sample was parallel to the rolling direction. As shown in FIG. 1, a deflection of y_0 was applied to the sample at a position of l = 50 mm as a working point to apply a stress (s) corresponding to 80% of the 0.2% yield strength in the rolling direction. The y_0 was determined by the following equation:

$$y_0 = (2 / 3)\cdot l^2\cdot s/(E\cdot t),$$

in which:

E is a Young's modulus in the rolling direction, and t is a thickness of the sample. The load was removed after heating at 300 °C for 10 hours, and an amount of permanent deformation (height) y was measured as shown in FIG. 2 to calculate the stress relaxation rate $\{[y\ (\mathrm{mm}) / y_0\ (\mathrm{mm})] \times 100\ (\%)\}$.

[0055] When the stress relaxation rate was 10% or less, the stress relaxation resistance was considered to be good (○).

[Table 1]

Examples	Production Conditions						Final Characteristics				
	Component (% by mass)		Hot Rolling		Final Solutionizing Treatment		YS (MPa)	Average Grain Size (μm)	Inverse Pole Figure in RD Direction		Stress Relaxation Property after 300 °C × 10h
	Ti	Additive Element	Compressive Strain per Pass (-)	Strain Rate of Final Pass (/s)	Temperature (°C)	Retention Time (s)			Pole Density of <111>	Higher Pole Density of <001> than <101>	
Example 1	3.3	0.15Fe	0.12	19.5	810	150	924	4	3.3	○	○
Example 2	3.3	0.15Fe	0.06	19.5	810	150	911	5	2.8	○	○
Example 3	3.3	0.15Fe	0.14	19.5	810	150	932	4	3.5	○	○
Example 4	3.3	0.15Fe	0.12	16.0	810	150	914	4	3.4	○	○
Example 5	3.3	0.15Fe	0.12	23.5	810	150	939	5	3.5	○	○
Example 6	3.3	0.15Fe	0.12	19.5	785	150	888	3	2.9	○	○
Example 7	3.3	0.15Fe	0.12	19.5	840	150	926	13	3.4	○	○
Example 8	3.3	0.15Fe	0.12	19.5	810	55	924	4	3.3	○	○
Example 9	3.3	0.15Fe	0.12	19.5	810	195	905	10	3.1	○	○
Example 10	3.3	-	0.12	19.5	810	150	897	24	3.2	○	○
Example 11	2.2	-	0.12	19.5	750	150	814	26	2.6	○	○
Example 12	4.3	-	0.12	19.5	865	150	1030	15	4.3	○	○
Example 13	3.3	0.15Mn-0.05Mo	0.08	18.6	810	150	967	5	3.2	○	○
Example 14	3.3	0.15Co-0.05Zr-0.05V	0.09	22.3	800	150	911	7	2.9	○	○
Example 15	3.3	0.1Zn-0.1Nb-0.1Si	0.11	22.1	800	150	884	9	3.3	○	○
Example 16	3.3	0.35Ni-0.1Mg	0.11	19.3	790	150	890	9	3.3	○	○

(continued)

Examples	Production Conditions						Final Characteristics				
	Component (% by mass)		Hot Rolling		Final Solutionizing Treatment		YS (MPa)	Average Grain Size (μm)	Inverse Pole Figure in RD Direction		Stress Relaxation Property after 300 °C × 10h
	Ti	Additive Element	Compressive Strain per Pass (-)	Strain Rate of Final Pass (/s)	Temperature (°C)	Retention Time (s)			Pole Density of <111>	Higher Pole Density of <001> than <101>	
Example 17	3.3	0.25Cr-0.05P	0.13	20.7	825	150	901	7	3.5	○	○
Example 18	3.3	0.15B	0.08	17.7	825	150	917	14	3.1	○	○
Comparative Example 1	3.3	0.15Fe	0.04	19.5	810	150	921	5	2.2	○	×
Comparative Example 2	3.3	0.15Fe	0.17	19.5	810	150	914	4	4.8	○	×
Comparative Example 3	3.3	0.15Fe	0.12	13.0	810	150	913	5	2.7	×	×
Comparative Example 4	3.3	0.15Fe	0.12	26.5	Not Produced		-	-		-	-
Comparative Example 5	3.3	0.15Fe	0.12	19.5	770	150	835	Non-recrystallized	5.4	○	×
Comparative Example 6	3.3	0.15Fe	0.12	19.5	850	150	834	38	2.1	○	×
Comparative Example 7	3.3	0.15Fe	0.12	19.5	810	40	929	Mixed Grain	4.4	×	×
Comparative Example 8	3.3	0.15Fe	0.12	19.5	810	220	846	32	2.7	×	×
Comparative Example 9	3.3	0.2Co-0.2Mn-0.2Zn	Not Produced					-		-	-

(continued)

Examples	Production Conditions						Final Characteristics				
	Component (% by mass)		Hot Rolling		Final Solutionizing Treatment		YS (MPa)	Average Grain Size (μm)	Inverse Pole Figure in RD Direction		Stress Relaxation Property after 300 °C × 10h
	Ti	Additive Element	Compressive Strain per Pass (-)	Strain Rate of Final Pass (/s)	Temperature (°C)	Retention Time (s)			Pole Density of <111>	Higher Pole Density of <001> than <101>	
Comparative Example 10	1.7	0.15Fe	0.12	19.5	725	150	789	18	2.2	×	×
Comparative Example 11	4.7	0.15Fe	Not Produced					-		-	-

[0056] In each of Examples 1 to 18, the stress relaxation rate after maintaining at 300 °C for 10 hours was 10% or less, indicating improved stress relaxation resistance.

[0057] On the other hand, in Comparative Example 1, the compressive strain per pass was too low and thus the pole density of <111> was lower than 2.5, so that an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained. In Comparative Example 2, the compressive strain per pass was too high, and thus the pole density of <111> was too much higher than 4.5, so that an improved stress relaxation resistance as compared with Invention Examples 1 to 18 could not be obtained.

[0058] In Comparative Example 3, the strain rate of the final pass was too low, so that the pole density of <001> has lower than that of <101 >, whereby an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained. In Comparative Example 4, the strain rate of the final pass was too high, so that the shape during rolling was poor, whereby the production was impossible.

[0059] In Comparative Example 5, the temperature of the final solutionizing treatment was too low, and thus the pole density of <111> was higher than 4.5, so that an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained. In Comparative Example 6, the temperature of the final solutionizing treatment was too high, and thus the pole density of <111> was lower than 2.5, so that an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained.

[0060] In Comparative Example 7, the retention time of the final solutionizing treatment was too short, so that the crystal grain size was of mixed grain type, and the pole density of <001> was lower than that of <101 >, whereby an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained. In Comparative Example 8, the retention time of the final solutionizing treatment was too long, the crystal grain size was coarsened, and the pole density of <001> was lower than that of <101 >, whereby an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained.

[0061] Comparative Examples 9 to 11 show cases where the addition amount of titanium or the third element was not appropriate. In Comparative Examples 9 and 11, the amounts of the additive element and titanium were too high, respectively, so that cracking occurred during hot rolling, and production was thus impossible. In Comparative Example 10, the addition amount of Ti was too low, so that the pole density of <111> was lower than 2.5 and the pole density of <001> was lower than that of <101>, whereby an improved stress relaxation resistance as compared with Examples 1 to 18 could not be obtained.

Claims

1. A titanium copper which contains from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, wherein a pole density of <111> is from 2.5 to 4.5, and a pole density of <001> is higher than that of <101 >, in an inverse pole figure in a rolling direction.

2. The titanium copper according to claim 1, wherein the titanium copper has a stress relaxation rate of 10% or less after maintaining the titanium copper at 300 °C for 10 hours.

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

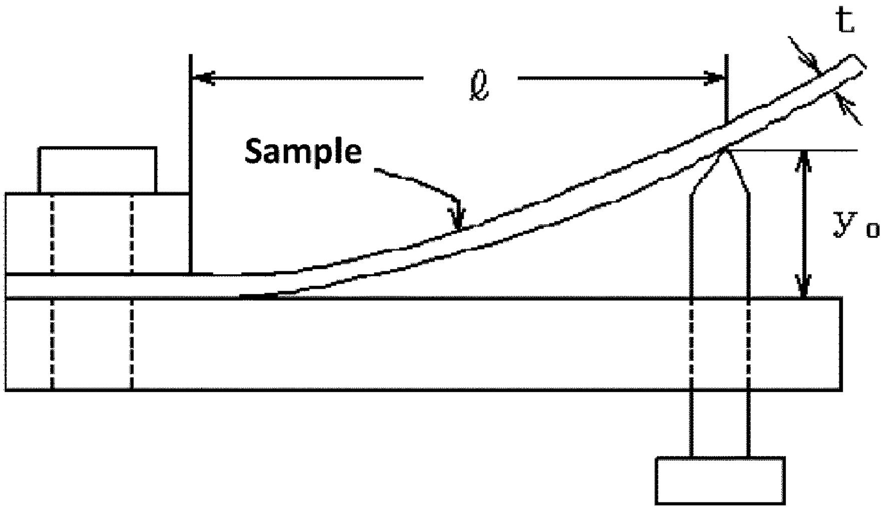
4. The titanium-copper according to any one of claims 1 to 3, wherein a 0.2% proof stress in a direction parallel to a rolling direction is 800 MPa or more when a tensile test is carried out according to JIS-Z2241 (2011).

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

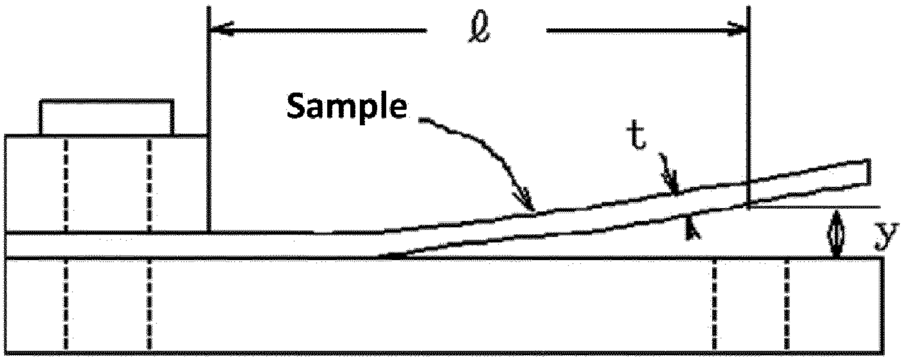
6. A method for producing titanium copper, the method comprising casting a titanium copper ingot containing from 2.0 to 4.5% by mass of Ti, and a total amount of from 0 to 0.5% by mass of at least one selected from the group consisting of Fe, Co, Ni, Cr, Zn, Zr, P, B, Mo, V, Nb, Mn, Mg, and Si as a third element, the balance being copper and inevitable impurities, and subjecting the cast ingot to hot rolling; and then carrying out a cold rolling step and a subsequent final solutionizing treatment step,
   wherein the hot rolling step comprises treating the ingot such that a compressive strain per pass is from 0.05 to 0.15 and a strain rate of a final pass is from 15.0 to 25.0/s, and
   wherein the final solutionizing treatment step comprises carrying out a treatment at a heating temperature (°C) of from $52 \times X + 610$ to $52 \times X + 680$ in which X is an addition amount (% by mass) of Ti, for a residence time of from

50 to 200 seconds.

[FIG. 1]



[FIG. 2]



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EUROPEAN SEARCH REPORT

Application Number
EP 19 20 2326

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 2 196 548 A1 (DOWA METALTECH CO LTD [JP]) 16 June 2010 (2010-06-16) * the whole document * -----	1-6	INV. C22C9/00 C22F1/08
A	US 2010/139822 A1 (GAO WEILIN [JP] ET AL) 10 June 2010 (2010-06-10) * the whole document * -----	1-6	

TECHNICAL FIELDS SEARCHED (IPC)
C22C C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	16 December 2019	Brown, Andrew

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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