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(54) Title: COPPER ALLOY

(57) Abstract: A copper alloy for electronic machinery and tools, containing Ni 2.0 to 4.5 mass%, and Si 0.3 to 1.0 mass%, with the balance being Cu and unavoidable impurities, which satisfies the following expression: I{311} x A / (I{311} + I{220} + I{200}) < 1.5 wherein I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and which has good bending property.

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DESCRIPTION

COPPER ALLOY

TECHNICAL FIELD

The present invention relates to an improved copper alloy on its properties.

BACKGROUND ART

In accordance with recent trends for miniaturizing and making electric and electronic machinery and tools of high performance, materials for components, such as connectors to be used therein, have been required to be improved in every characteristics strictly. Concretely, for example, the thickness of a sheet to be used at the contact point of a spring of a connector, has become so thin that it is difficult to ensure sufficient contact pressure. That is, in the contact point of a spring of a connector, generally, a contact pressure required for electrical connection is obtained from counterforce obtained by previously deflecting a sheet (a spring sheet). Therefore, a larger degree of deflecting is needed to obtain the same degree of contact pressure when the sheet is thinned. However, the sheet may undergo plastic deformation when the deflecting degree exceeds the elasticity limit of the sheet. Accordingly, additional improvements of the elasticity limit of the sheet have been required.

A variety of other characteristics, such as stress relaxation resistance, heat conductivity, bending property, heat resistance, plate adhesion property, and migration resistant property, have also been required for the material of the spring contact point of the connector. Mechanical strength, stress relaxation resistance, heat and electric conductivity, and bending property are important, among the various characteristics. While phosphor bronze has been frequently used for the

spring contact point of the connector, it cannot completely satisfy the requirements described above. Accordingly, phosphor bronze is being replaced by a low-beryllium-copper alloy (an alloy prescribed in JIS C 1753) in recent years, which has higher mechanical strength and a good stress relaxation resistance, as well as good electric conductivity.

There is known a Cu-Ni-Si-based alloy as an example of the contact member material having properties comparable to those of low beryllium copper and having a relatively high strength as an inexpensive and highly safe material. Another example of the contact member material includes a copper alloy having improved in its stress relaxation resistance, which is obtained by adding Mg to the Cu-Ni-Si-based alloy. Still another example of the contact member material includes a copper alloy having mechanical strength comparable to that of low beryllium copper, which is obtained by increasing Ni and Si amounts of the Cu-Ni-Si-based alloy.

However, low beryllium copper has problems in that it is very expensive and that metal beryllium has toxicity. Attempts have been made to enhance the strength of the Cu-Ni-Si-based alloy. However, excessive increase in Ni and Si amounts in the copper alloy degrades bending property, which is one of the properties required to a connector, and restricts possible applications of the connector. To be specific, intergranular embrittlement cracking of the copper alloy occurs during bending, resulting in degrading of the bending property of the copper alloy. Thus, no Cu-Ni-Si-based alloy having the strength, electrical conductivity, and bending property comparable to those of low beryllium copper has been found. Further, even if Mg is added to the Cu-Ni-Si-based alloy, the stress relaxation resistance comparable to that of low beryllium copper has not been obtained.

Other and further features and advantages of the invention will appear more fully from the following description.

DISCLOSURE OF INVENTION

According to the present invention, there is provided the following means:

[1] A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, and Si 0.3 to 1.0 mass%, with the balance being Cu and unavoidable impurities,

which satisfies the following expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

[2] A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, and S more than 0 and less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies the following expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

[3] The copper alloy according to the above item [1] or [2], which further comprises Zn 0.2 to 1.5 mass%.

[4] The copper alloy according to any one of the above items [1] to [3], which

further comprises Mg 0.01 to 0.2 mass%.

[5] The copper alloy according to any one of the above items [1] to [4], which further comprises Sn 0.05 to 1.5 mass%.

[6] A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Mg 0.01 to 0.2 mass%, Sn 0.05 to 1.5 mass%, Zn 0.2 to 1.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies the following expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

[7] The copper alloy according to any one of the above items [1] to [6], which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, and B 0.001 to 0.02 mass%, in a total content of 0.001 to 2.0 mass%.

[8] A copper alloy, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Cr 0.1 to 0.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies the following expression (2):

$$I\{311\} / (I\{311\} + I\{220\} + I\{200\}) < 0.15 \quad \cdots(2)$$

wherein, in expression (2), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; and I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface.

[9] A copper alloy, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Cr 0.1 to 0.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies the following expression (3):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(3)$$

wherein, in expression (3), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size.

[10] The copper alloy according to the above item [8] or [9], which further comprises Zn 0.2 to 1.5 mass%.

[11] The copper alloy according to any one of the above items [8] to [10], which further comprises Mg 0.01 to 0.2 mass%.

[12] The copper alloy according to any one of the above items [8] to [11], which further comprises Sn 0.05 to 1.5 mass%.

[13] The copper alloy according to any one of the above items [8] to [12], which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, Ti 0.005 to 0.3 mass%, Ag 0.005 to 0.3 mass%, and B 0.001 to 0.02 mass%.

Hereinafter, a first embodiment of the present invention means to include the copper alloys described in the items [1] to [7] above.

A second embodiment of the present invention means to include the copper alloys described in the items [8] to [13] above.

Herein, the present invention means to include both of the above first and second embodiments, unless otherwise specified.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is explained in detail below.

[First Embodiment]

According to the first embodiment, can be improved bending property of a copper alloy, which contains a Ni-Si compound precipitated in Cu matrix and which has moderate mechanical strength and electrical conductivity, by strictly controlling an integration degree of crystal orientations and a crystalline grain size.

Hereinafter, a relationship among the crystal orientations of the copper alloy of the first embodiment (hereinafter, simply referred to as a first copper alloy) will be described. Regarding a copper alloy containing Ni and Si, the inventors of the present invention have found that the integration degree of the crystal orientations can be determined by controlling X-ray diffraction intensities and that the copper alloy is improved in bending property and mechanical strength by satisfying an expression derived from the X-ray diffraction intensities. That is, bending property and mechanical strength of the copper alloy can be improved, when the copper alloy satisfies the following expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size.

In the above expression (1), the relationship between the integration degree of crystal orientations and the crystalline grain size is defined to give a value of less than 1.5, preferably less than 1.2. A lower limit of the value is not particularly limited, but is generally more than 0.3. Too large a value inhibits improvements in both the bending property and mechanical strength of the copper alloy. A copper alloy containing Ni and Si recrystallizes and increases its grain size, to thereby increase integration ratios of the {200} and {311} planes to

the sheet surface. The copper alloy is subjected to cold rolling at a higher reduction rate, to thereby further increase the integration ratio of the {220} plane to the sheet surface. A relationship between the integration degree of the crystal orientations and the X-ray diffraction intensity is that a high X-ray diffraction intensity provides a high integration degree of the crystal orientations. Herein, an integration ratio of an X-ray diffraction plane (an integration degree of crystal orientations) refers to a ratio of crystal growth rate in a direction of each diffraction plane, and may be evaluated as a ratio of an X-ray diffraction intensity (I) of each diffraction plane. In the present invention, the integration ratio of the X-ray diffraction plane is represented by the left side of the expression (1) (A = 1, in this case). The first copper alloy can be produced, for example, through steps of "hot rolling", "cold rolling", "solution treatment", and "aging treatment", and additional steps of "finish cold rolling" and "distortion elimination annealing" if necessary. The integration degree of the crystal orientations and the crystalline grain size vary depending on a combination of a reduction rate before the solution treatment, conditions for the solution treatment, and a reduction rate in cold working. In the present invention, to improve the bending property of the copper alloy by suppressing intergranular embrittlement of the copper alloy upon bending when Ni and Si amounts are increased in particular, the present inventors provide an appropriate range with the expression (1) to define the relationship between the integration degree of crystal orientations and the crystalline grain size.

The alloy elements in the first copper alloy will be described hereinafter.

When Ni and Si are added into Cu, a Ni-Si-series compound (a Ni_2Si phase) is precipitated in Cu matrix, to improve mechanical strength and electric conductivity. The content of Ni is defined in the range of 2.0 to 4.5% by mass. This is because a mechanical strength in the same level of or superior to that of the conventional low-beryllium copper cannot be obtained when the Ni content is less than 2.0% by mass. On the other hand, when the Ni content exceeds 4.5%

by mass, precipitation that does not contribute to the improvement in mechanical strength are occurred during casting or hot-working, not only to fail in obtaining a mechanical strength rewarding the amount of Ni to be added, but also to cause problems of adversely affecting hot-working property and bending property. The Ni content is preferably 2.2 to 4.2% by mass, more preferably 3.0 to 4.0% by mass.

Since Si forms a Ni_2Si phase together with Ni, the amount of Si to be added is determined by determining the amount of Ni. Mechanical strength in the same level of or superior to that of the low-beryllium copper cannot be obtained when the Si content is less than 0.3% by mass, similarly in the case when the content of Ni is too small. When the content of Si exceeds 1.0% by mass, on the other hand, the same problems arise as in the case when the content of Ni is too large. The Si content is preferably 0.5 to 0.95% by mass, more preferably 0.7 to 0.9% by mass.

The mechanical strength varies depending on the contents of Ni and Si, and stress relaxation resistance is also changed accordingly. Therefore, the contents of Ni and Si should be strictly controlled within the range as defined in this embodiment, in order to obtain a stress relaxation resistance in the same level of or superior to that of the low-beryllium copper. In addition, the contents of Mg, Sn and Zn, the crystal grain diameter, and the shape of crystal grain as will be described later, should be also appropriately controlled.

Mg, Sn and Zn are important alloy elements that constitute the copper alloy of the present invention. These elements in the alloy are correlated with each other, to realize various excellent characteristics well-balanced.

Mg largely improves stress relaxation resistance, but it adversely affects bending property. The more the content of Mg is, the more the stress relaxation resistance is improved, provided that the Mg content is, for example, 0.01% by mass or more. However, if the Mg content is too large, the resultant bending

property cannot satisfy the required level. It is preferable that the content of Mg is strictly controlled in the present invention in the case of adding Mg, since precipitation of the Ni_2Si phase far more contribute to the degree of reinforcement as compared with the conventional Cu-Ni-Si-series alloys, thereby bending property is apt to be poor. The content of Mg is generally 0.01 to 0.2% by mass, preferably 0.05 to 0.15% by mass.

Sn is able to more improve stress relaxation resistance, mutually correlated with Mg. However, such an improving effect of Sn is not so large as Mg. Sufficient effects for adding Sn cannot be sufficiently appeared when the Sn content is too low, while, when the Sn content is too large, electric conductivity decreases conspicuously. The content of Sn is generally 0.05 to 1.5% by mass, preferably 0.1 to 0.7% by mass.

Zn a little improves bending property. Zn content is generally in the range of 0.2 to 1.5% by mass. When Zn is added in the defined range of 0.2 to 1.5% by mass, bending property in the practically non-problematic level can be achieved, even by adding Mg in maximum 0.20% by mass. In addition, Zn improves adhesion property of Sn plate or solder plate, as well as migration resistant characteristics. The effect of adding Zn cannot be sufficiently obtained when the Zn content is too low, while, when the Zn content is too large, electric conductivity decreases. The content of Zn is preferably 0.3 to 1.0% by mass.

Sub-component elements, such as Co and Zr, that are effective for improving mechanical strength, will be described hereinafter.

Co forms a compound with Si as Ni does, to improve mechanical strength. The content of Co is generally 0.05 to 2.0% by mass. The effect of adding Co cannot be sufficiently obtained when the Co content is too small, while, when the Co content is too large, bending property is apt to be degraded. The content of Co is generally 0.05 to 2.0% by mass, preferably 0.1 to 1.0% by mass.

Zr finely precipitates in copper, to thereby contribute to enhancing

mechanical strength of the resultant copper alloy and provide an effect of reducing the integration degree of the crystal orientations represented in the expression (1). The effect of adding Zr cannot be sufficiently obtained when the Zr content is too small, while, when the Zr content is too large, bending property is apt to become degraded. From the above viewpoint, the content of Zr is generally 0.005 to 0.3% by mass, preferably 0.05 to 0.2% by mass.

The sum total content of Co, Zr and B when at least two kinds of these elements are simultaneously contained in the alloy, is determined to be within the range of generally 0.001 to 2.0% by mass, preferably 0.005 to 2.0% by mass, depending on the required characteristics. B forms a compound with Ni, to thereby reduce the integration degree of the crystal orientations represented in the expression (1). The effect of adding B cannot be sufficiently obtained when the B content is too small, while, when the B content is too large, hot-workability is apt to be degraded. From the above viewpoint, the content of B is generally 0.001 to 0.02% by mass, preferably 0.005 to 0.01% by mass.

The copper alloy generally contains a trace amount of S. When an S content is too high, it results degraded hot-workability. Thus, the S content is preferably defined to be less than 0.005 mass%, particularly preferably less than 0.002 mass%.

In the present invention, it is possible to add other elements, such as Fe, P, Mn, Ti, V, Pb, Bi and Al in an appropriate amount in an extent not degrading essential characteristics such as mechanical strength and electric conductivity. For example, Mn has an effect to improve hot-working property, and it is effective to add Mn in the range of 0.01 to 0.5% by mass, so as not to degrade electric conductivity.

The copper alloy containing Ni and Si recrystallizes and increases its grain size, to thereby increase the integration ratios of the {200} and {311} planes to the sheet surface. The copper alloy is subjected to rolling, to thereby increase

the integration ratio of the {220} plane to the sheet surface.

The first copper alloy can be produced through, for example, the steps of hot rolling, cold rolling, solution treatment, and aging treatment, and further additional steps of finish cold rolling and distortion elimination annealing, as required. In the production steps, for example, the conditions of hot rolling (temperature and period of time), subsequent cold rolling and solution treatment (temperatures and periods of time), and subsequent cold rolling (reduction rate) are strictly controlled to narrower ranges than those of general conditions. Thus, the integration ratios and the crystalline grain size of the copper alloy can be controlled, to thereby satisfy the expression (1).

In the production of the first copper alloy, specifically, the expression (1) can be satisfied, for example, by adjusting a temperature of hot rolling within a range of 900 to 1,000°C, a reduction rate of cold rolling after the hot rolling to 90% or more, a temperature of solution treatment to 820 to 930°C for 20 sec or less, and a reduction rate of the subsequent cold rolling to 30% or less.

The direction of final plastic working as used herein refers to the direction of rolling when the rolling is the finally carried out plastic working, or to the direction of drawing when the drawing (linear drawing) is the plastic working finally carried out. The plastic working refers to rolling and drawing, but working for the purpose of leveling (vertical leveling) using, for example, a tension leveler, is not included in this plastic working.

[Second Embodiment]

According to the second embodiment, the Cu-Ni-Si-based alloy is modified through the following means to satisfy recent needs, and the bending property and mechanical strength of the copper alloy containing an Ni-Si compound precipitated in Cu matrix can be improved by controlling a Cr amount and the integration degree of crystal orientations.

Each component element of the copper alloy of the second embodiment (hereinafter, simply referred to as a second copper alloy) will be described.

It is known that a Ni-Si-series compound (a Ni_2Si phase) is precipitated in Cu matrix by adding Ni and Si in Cu, to improve mechanical strength and electric conductivity. In the present invention, the content of Ni is generally in the range of 2.0 to 4.5% by mass, preferably in the range of 2.2 to 4.2% by mass, and more preferably in the range of 3.0 to 4.0% by mass.

The content of Ni is defined as above. This is because a mechanical strength in the same level of or superior to that of the conventional beryllium-copper alloy cannot be obtained when the Ni content is too low. On the other hand, when the Ni content is too high, precipitation that does not contribute to the improvement in mechanical strength are precipitated during casting or hot-working, not only to fail in obtaining a mechanical strength rewarding the amount of Ni to be added, but also to cause problems of adversely affecting hot-working property and bending property.

Since Si form a Ni_2Si phase together with Ni, the optimum amount of Si to be added is determined by determining the amount of Ni. The Si content is generally 0.3 to 1.0% by mass, preferably 0.5 to 0.95% by mass, and more preferably 0.7 to 0.9% by mass. Mechanical strength in the same level of or superior to that of the beryllium-copper alloy cannot be obtained when the Si content is too small, similarly in the case when the content of Ni is too small. When the content of Si is too large, on the other hand, the same problems arise as in the case when the content of Ni is too large.

The content of Cr and the X-ray diffraction intensity of the resulting copper alloy are controlled, to thereby improve the bending property and mechanical strength of an alloy sheet material.

That is, both the bending property and the mechanical strength of the alloy sheet material are improved, by adjusting a Cr content to 0.1 to 0.5 mass%

and satisfying an expression (2) or (3) described below.

Further, Cr is present in the alloy as a Cr compound such as Cr-Si-series or Cr-Ni-Si-series, and it has an effect of suppressing increase of the crystalline grain size during the solution treatment and an effect of reducing the integration degree of the crystal orientations represented in the expression. However, too low a Cr content provides insufficient effect, and too high a Cr content degrades the bending property of the alloy. From those viewpoints, the Cr content is generally 0.1 to 0.5 mass%, preferably 0.15 to 0.4 mass%.

Mg, Sn and Zn are important alloy elements that constitute the copper alloy of the present invention. These elements in the alloy are correlated with each other, to realize various excellent characteristics well-balanced.

Mg improves stress relaxation resistance, but it adversely affects bending property. The more the content of Mg is, the more the stress relaxation resistance is improved, provided that the Mg content is, for example, 0.01% by mass or more. However, the resultant bending property cannot satisfy the required level, if the Mg content is too large. It is preferable that the content of Mg is strictly controlled in the present invention in the case of adding Mg, since precipitation of the Ni_2Si phase far more contribute to the degree of reinforcement as compared with the conventional Cu-Ni-Si-series alloys, thereby bending property is apt to be poor. The content of Mg is generally 0.01 to 0.2% by mass, preferably 0.05 to 0.15% by mass.

Sn is able to more improve stress relaxation resistance, mutually correlated with Mg. Sufficient effects for adding Sn cannot be sufficiently appeared when the Sn content is too small, while, when the Sn content is too large, electric conductivity decreases conspicuously. The content of Sn is generally 0.05 to 1.5% by mass, preferably 0.1 to 0.7% by mass.

Zn can improve bending property. The Zn content is generally 0.2 to 1.5% by mass, and by adding Zn, bending property in the practically non-

problematic level can be achieved, even by adding Mg in maximum 0.20% by mass. In addition, Zn improves adhesion property of Sn plate or solder plate, as well as migration resistant characteristics. The effect of adding Zn cannot be sufficiently obtained when the Zn content is too small, while, when the Zn content is too large, electric conductivity decreases. The content of Zn is preferably 0.3 to 1.0% by mass.

Zr, Co, Ti, Ag, and B each have an effect of reducing the integration degree of the crystal orientations represented in any of the expressions described below.

Zr has an effect of reducing the integration degree of the crystal orientations represented in the expression and contributes to enhancing the strength of the alloy at the same time. Too low a Zr content provides insufficient effect, and too high a Zr content degrades the bending property of the alloy. From those viewpoints, the Zr content is generally 0.005 to 0.3 mass%, preferably 0.05 to 0.2 mass%.

Co forms a compound with Si to improve the strength of the alloy, similar to Ni, and has an effect of reducing the integration degree of the crystal orientations represented in the expression. The content of Co is generally 0.05 to 2.0% by mass. The effect of adding Co cannot be sufficiently obtained when the Co content is too small, while, when the Co content is too large, bending property degrades. The content of Co is preferably 0.1 to 1.0% by mass.

Similar to Cr, Zr, Ti, Ag, and other elements, Co has effects of suppressing increase of the crystalline grain size and reducing the integration degree of crystal orientations of the expression.

B has an effect of reducing the integration degree of the crystal orientations represented in the expression. Too low a B content provides insufficient effect, and too high a B content degrades hot-workability. From those viewpoints, the B content is generally 0.001 to 0.02 mass%, preferably 0.005 to

0.1 mass%.

Ti improves heat resistance and mechanical strength of the alloy, and has effects of suppressing increase of the crystalline grain size and reducing the integration degree of the crystal orientations represented in the expression. Too low a Ti content provides insufficient effect; while too high a Ti content leaves undissolved Ti remained, provides no effect, and has adverse affects on plating properties or the like. From those viewpoints, the Ti content is generally 0.005 to 0.3 mass%, preferably 0.05 to 0.2 mass%.

Ag improves heat resistance and mechanical strength of the alloy, and has effects of suppressing increase of the crystalline grain size and reducing the integration degree of crystal orientations represented in the expression. If the amount of Ag is too small, it results in insufficient effect of adding Ag; while if the amount of Ag is too large, it results in a high manufacturing cost of the alloy, although no adverse affects on resulting characteristics are observed at such a high Ag amount to be added. From the viewpoints in the above, the Ag content is generally 0.005 to 0.3% by mass, preferably 0.05 to 0.2% by mass.

It is more preferable that the sum total content of Co, Zr, Ti, Ag and B when at least two kinds of these elements are simultaneously contained in the alloy, is defined to be within the range of 0.005 to 2.0% by mass, depending on the required characteristics.

The copper alloy generally contains a trace amount of S. When an S content is too high, it results degraded hot-workability. Thus, the S content is preferably defined to be less than 0.005 mass%, particularly preferably less than 0.002 mass%.

In the present invention, it is possible to add other elements, such as Fe, P, Mn, V, Pb, Bi and Al, in an appropriate amount, in an extent not degrading essential characteristics such as mechanical strength and electric conductivity. For example, Mn has an effect to improve hot-working property, and it is effective

to add Mn in the range of 0.01 to 0.5% by mass, so as not to decrease electric conductivity.

Next, the crystal orientations of the second copper alloy will be described.

In the copper alloy containing Ni and Si, the resultant crystal recrystallizes and increases its grain size, to thereby increase the integration ratios of the {200} and {311} planes to the sheet surface. The copper alloy is subjected to rolling, to thereby increase the integration ratio of the {220} plane to the sheet surface.

The second copper alloy can be produced, for example, through the steps of hot rolling, cold rolling, and aging treatment, and further additional steps of finish cold rolling and distortion elimination annealing, as required. In the production steps, for example, the conditions of hot rolling (temperature and period of time), subsequent cold-rolling and solution treatment (temperatures and periods of time), and subsequent cold-rolling (reduction rate) are strictly controlled to narrower ranges than those of general conditions, to thereby allow controlling of the integration ratios and the crystalline grain size.

The inventors of the present invention have found that the copper alloy having the integration degree of the crystal orientations, which are determined from the X-ray diffraction intensities showing the integration ratios, within a specific range, is improved in bending property and mechanical strength. Herein, the integration ratio of the X-ray diffraction plane (the integration degree of the crystal orientations) refers to a ratio of crystal growth degree in a direction of each diffraction plane, and may be evaluated as a ratio of an X-ray diffraction intensity (I) of each diffraction plane. To be specific, the copper alloy satisfying the following expression (2) and having a Cr content within the above specific range can have improved bending property and mechanical strength:

$$I\{311\} / (I\{311\} + I\{220\} + I\{200\}) < 0.15 \quad \cdots(2)$$

wherein I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220}

plane at the sheet surface; and I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface.

In the above expression (2), the integration degree of the crystal orientations is a value of less then 0.15, preferably less then 0.12. A lower limit of the value is not particularly limited, but is generally more than 0.03. If this value is too large, it results in inhibition of improvement in both the bending property and mechanical strength of the copper alloy.

Further, the copper alloy satisfying the following expression (3) can have improved bending property and tensile strength:

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(3)$$

wherein, similar to the above, I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size.

In the above expression (3), the relationship between the integration degree of crystal orientations and the crystalline grain size is defined to give a value of less than 1.5, preferably less than 1.2. A lower limit of the value is not particularly limited, but is generally more than 0.3. Similarly to the above, too large this value inhibits improvements in both the bending property and the mechanical strength of the copper alloy. Thus, the crystalline grain size is preferably as small as possible, and specifically, the grain size is preferably less than 10 μm, more preferably 5 to 8 μm.

In the production of the second copper alloy, the expression (2) or (3) can be satisfied by specifically adjusting, for example, a temperature of hot rolling within a range of 900 to 1,000°C, a reduction rate of cold rolling after the hot rolling to 90% or more, a temperature of solution treatment to 820 to 930°C for 20 sec or less, and a reduction rate of the subsequent cold rolling to 30% or less.

According to the present invention, can be provided a copper alloy having, for example, excellent mechanical strength, electrical conductivity and bending property, and in some cases in addition to these, excellent stress relaxation resistance and plate adhesion, as a material for a terminal, a connector, a switch, or the like.

The copper alloy of the present invention is excellent, for example, in mechanical strength, electrical conductivity, and bending property (the above first embodiment), and further in stress relaxation resistance (the above second embodiment) in addition to the above. A copper alloy material obtained by working the copper alloy can be applied to production of small, high performance parts of electric and electronic machinery and tools. The copper alloy of the present invention can be preferably applied, for example, to terminal, connector, or switch, as well as general conductive materials for lead frame, relay, or the like.

EXAMPLES

The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these. In the following examples, Examples 1 and 2 correspond to examples of the first embodiment, and Examples 3 and 4 correspond to examples of the second embodiment.

(Example 1)

Copper alloys each having the composition, as shown in Table 1 (Ingot Nos. A to V, WA to WH, X and Z), each were melted in a high-frequency melting furnace, to cast into ingots with thickness 30 mm, width 100 mm and length 150 mm, by a DC method, respectively. Then, these ingots were heated to 1,000°C. After holding the ingots at this temperature for 1 hour, the resultant ingots each were hot-rolled to a sheet with thickness 12 mm, followed by rapid cooling.

Then, both end faces of the hot-rolled sheet each were cut (chamfered) by 1.5 mm, to remove an oxide film on each side. The resultant sheet was worked into a sheet of thickness 0.15 to 0.25 mm through cold rolling (a). Then, the cold-rolled sheet was subjected to heat treatment for 15 sec while a temperature of solution treatment was changed within the range of 825 to 925°C, after that, immediately followed by cooling at a cooling rate of 15°C/sec or more. Then, aging treatment was carried out at 475°C for 2 hours in an inert gas atmosphere, and then, depending on the samples, if necessary, cold rolling (c) as a final plastic working was carried out, to adjust to the final sheet thickness of 0.15 mm. After the aging treatment or final plastic working, the samples were then subjected to low-temperature annealing at 375°C for 2 hours, thereby manufacturing copper alloy sheets (Sample Nos. 1 and 5 to 41), respectively.

(Example 2)

Copper alloy sheets with thickness 0.15 mm were manufactured by working, in the following conditions, the copper alloys (Ingot No. J) of the composition, as shown in Table 1, respectively. That is, the manufacturing conditions were the same as the manufacturing steps in Example 1, from the beginning with the melting to the elimination of oxide films after the hot-rolling. Then, the resultant sheets were worked by cold-rolling (a) to thickness 0.15 to 0.5 mm, followed by heat-treating for 15 seconds at a solution treatment temperature within the range of 825 to 925°C. The sheets were, thereafter, immediately cooled at a cooling rate of 15°C/sec or more.

Then, depending on the samples, if necessary, the resultant sheets were subjected to cold-rolling (b) at a reduction rate of 50% or less, and then, in the same conditions as in Example 1, the aging treatment in an inert gas atmosphere, the final plastic working (cold-rolling (c), to a final sheet thickness of 0.15 mm), and then the low-temperature annealing, thereby manufacturing the copper alloy

sheets (Sample Nos. 2 to 4), respectively.

Table 1

Ingot No.	Ni mass%	Si mass%	Mg mass%	Sn mass%	Zn mass%	S mass%	Other elements mass%
A	3.8	0.89	-	-	-	0.002	-
B	3.4	0.83	-	-	-	0.002	-
C	3.2	0.77	-	-	-	0.002	-
D	3.8	0.9	0.1	-	-	0.002	-
E	3.8	0.9	-	0.15	-	0.002	-
F	3.8	0.9	-	-	0.5	0.002	-
G	3.8	0.9	0.1	0.15	-	0.002	-
H	3.8	0.9	0.1	-	0.5	0.002	-
I	3.8	0.9	-	0.15	0.5	0.002	-
J	3.8	0.9	0.1	0.15	0.5	0.002	-
K	3.5	0.84	0.1	0.16	0.47	0.002	-
L	3.3	0.78	0.1	0.16	0.48	0.002	-
N	3.8	0.89	0.1	0.15	0.5	0.002	Zr:0.1
O	3.8	0.89	0.1	0.15	0.5	0.002	Co:0.25
P	3.8	0.89	0.1	0.15	0.49	0.002	B:0.01
Q	5	1.17	0.1	0.21	0.49	0.002	-
R	3.8	0.9	0.1	0.15	1.7	0.002	-
S	3.8	0.9	0.38	0.2	0.5	0.002	-
T	3.8	0.89	0.08	2.01	0.5	0.002	-
V	4.1	0.9	0.1	0.15	0.48	0.002	B:0.03
WA	2.3	0.56	-	-	-	0.002	-
WB	2.3	0.56	0.1	-	-	0.002	-
WC	2.2	0.54	-	0.15	-	0.002	-
WD	2.3	0.56	-	-	0.5	0.002	-
WE	2.4	0.55	0.1	0.15	-	0.002	-
WF	2.3	0.56	0.1	-	0.5	0.002	-
WG	2.4	0.55	-	0.15	0.5	0.002	-
WH	2.3	0.56	0.1	0.15	0.5	0.002	-
X	3.8	0.9	0.1	0.15	0.5	0.011	-
Z	1.7	0.27	0.1	0.15	0.5	0.002	-

Note: The balance of each alloy was copper and unavoidable impurities; "-" not added.

The thus-manufactured copper alloy sheets each were tested and

evaluated with respect to (1) crystal grain diameter, (2) crystal orientation, (3) tensile strength, (4) electric conductivity, and (5) bending property.

The crystal grain diameter (1) was measured according to JIS H 0501 (a cutting method).

The crystal orientations (2) were determined by: irradiating a surface of the copper alloy sheet of a final product state (thickness 0.15 mm) with X-rays; and measuring intensities from diffraction planes. Of those, diffraction intensities of the {200}, {220}, and {311} planes each showing a strong correlation with the bending property were compared, to thereby obtain a crystal orientation intensity ratio (I{311}×A/(I{311}+I{220}+I{200})). The conditions for the X-ray irradiation were: X-ray source CuKα1; tube voltage 40 kV; and tube current 20 mA.

The tensile strength (3) was determined according to JIS Z 2241, using #5 test pieces described in JIS Z 2201, which were formed from each of the sample sheets.

The electric conductivity (4) was determined according to JIS H 0505.

The bending property (5) was evaluated based on a method described in JIS H 3110. A test piece with width 10 mm was bent at a load of 1,000 kgf. The test piece was cut out in a GW direction (with a bending axis perpendicular to the rolling direction) or a BW direction (with a bending axis parallel to the rolling direction). The bending property was evaluated with a ratio R/t, in which R represents a minimum bending radius at a limit of crack formation and t represents a thickness of the test piece.

As is apparent from the results shown in Table 2, the sample Nos. 1, 5 to 19 (Example 1) and the sample Nos. 2 to 4 (Example 2) each had excellent characteristics satisfying all of a bending property (R/t) of less than 2, a tensile strength of 800 MPa or more, and an electrical conductivity of 35%IACS or more. Further, the sample Nos. 34 to 41 had a slightly low tensile strength, but each had excellent properties satisfying a bending property (R/t) of less than 2 and an

electrical conductivity of 35%IACS or more.

In contrast, the sample Nos. 20 to 25 (comparative examples) each had a value of the expression (1) falling outside of the range defined in the present invention, and had conspicuously poor bending property, which was presumably caused since the temperature of the solution treatment was too high.

The sample No. 26 (comparative example) could not be normally produced, since cracks were occurred during the hot-working, due to the too large contents of Ni and Si.

The sample No. 27 (comparative example for the invention according to the above item [3]) satisfied the value of the expression (1) and had excellent bending property. However, due to a too high Zn content, this sample was poor in electrical conductivity.

The sample No. 28 (comparative example for the invention according to the above item [4]) was poor in bending property, due to a too high Mg content.

The sample No. 29 (comparative example for the invention according to the above item [5]) could not be produced, since during the cold-rolling were occurred edge cracks, due to a too high Sn content.

The sample No. 31 (comparative example for the invention according to the above item [7]) could not be normally produced, since cracks were occurred during the hot-working, due to a too high B content.

Production of the sample of No. 32 (comparative example for the invention according to the above item [2]) was stopped, since cracks occurred during hot-working, due to too large content of S.

The sample No. 33 provided a value of the expression (1) falling outside of the range defined in the present invention. This sample had too small Ni and Si contents, was poor in mechanical strength and fell largely short of beryllium copper.

Table 2

	Ingot No	Sample No	Value of expression (1)	Bending property (R/t)		Tensile strength	Electric conductivity
				GW	BW	MPa	%IACS
This invention	A	5	0.67	1.0	1.0	815	39
	B	6	0.71	1.0	1.0	820	39
	C	7	0.61	1.0	1.0	820	40
	D	8	0.63	1.5	1.5	810	38
	E	9	0.66	1.0	1.0	815	37
	F	10	0.61	1.0	1.0	820	38
	G	11	0.6	1.5	1.5	810	37
	H	12	0.57	1.0	1.0	825	38
	I	13	0.58	1.0	1.0	820	37
	J	1	0.99	1.0	1.0	810	36
	J	2	0.57	1.0	1.0	820	36
	J	3	0.54	1.5	1.5	860	36
	J	4	0.4	1.0	1.0	820	37
	K	14	1.18	1.0	1.0	820	37
	L	15	1.23	1.0	1.0	825	38
	N	17	0.6	1.0	1.0	810	35
	O	18	0.46	1.0	1.0	815	36
	P	19	0.56	1.0	1.0	805	36
	WA	34	0.43	0.5	0.5	734	42
	WB	35	0.44	0.5	0.5	743	40
	WC	36	0.63	0.75	0.5	732	39
	WD	37	0.54	0.5	0.5	724	40
	WE	38	0.5	0.5	0.5	722	37
	WF	39	0.41	0.75	0.5	741	38
	WG	40	0.61	0.5	0.5	735	37
	WH	41	0.96	0.5	0.5	720	36
Comparative Example	J	20	6.06	2.0	2.0	820	35
	J	21	4.12	2.5	2.5	825	35
	J	22	3.06	3.5	3.5	855	35
	J	23	1.7	3.0	3.0	850	36
	K	24	2.96	2.5	2.5	825	37
	L	25	3.12	2.5	2.5	830	34
	Q	26	Cracks during hot-working				
	R	27	0.65	1.0	1.0	820	30
	S	28	0.71	2.0	2.0	815	33
	T	29	Cracks during cold-working				
	V	31	Cracks during hot-working				
	X	32	Cracks during hot-working				
	Z	33	3.96	1.0	1.0	644	41

(Example 3)

Copper alloys each having the composition, as shown in Table 3 (Ingot Nos. 2-A to 2-O, 2-PA to 2-PH, 2-Q to 2-S, 2-Z and 2-A-1), each were melted in a high-frequency melting furnace, to cast into ingots with thickness 30 mm, width 100 mm and length 150 mm, by a DC method, respectively. Then, these ingots were heated to 1,000°C. After holding the ingots at this temperature for 1 hour, the resultant ingots each were hot-rolled to a sheet with thickness 12 mm, followed by rapid cooling.

Then, both end faces of each of the hot-rolled sheets each were cut (chamfered) by 1.5 mm, to remove oxide layers. The resultant sheets were worked to thickness 0.15 to 0.25 mm by cold rolling (2-a). Then, the cold-rolled sheets were heat-treated for 15 seconds with varying a solution treatment temperature in the temperature range of 825 to 925°C, after that, immediately followed by cooling at a cooling rate of 15°C/sec or more. Then, aging treatment was carried out at 475°C for 2 hours in an inert gas atmosphere, and then, depending on the samples, if necessary, cold rolling (2-c) as a final plastic working was carried out, to adjust to the final sheet thickness of 0.15 mm. After the aging treatment or final plastic working, the samples were then subjected to low-temperature annealing at 375°C for 2 hours, thereby manufacturing copper alloy sheets (Sample Nos. 2-0 to 2-2, 2-1-1 and 2-5 to 2-30), respectively.

(Example 4)

Copper alloy sheets with thickness 0.15 mm were manufactured by working, in the following conditions, the copper alloys (Ingot No. 2-B) of the composition, as shown in Table 3, respectively. That is, the manufacturing conditions were the same as the manufacturing steps in Example 3, from the beginning with the melting to the elimination of oxide films after the hot-rolling. Then, the resultant sheets were worked by cold-rolling (2-a) to thickness 0.15 to

0.5 mm, followed by heat-treating for 15 seconds at a solution treatment temperature within the range of 825 to 925°C. The sheets were, thereafter, immediately cooled at a cooling rate of 15°C/sec or more. Then, depending on the samples, if necessary, the resultant sheets were subjected to cold-rolling (2-b) at a reduction rate of 50% or less, and then, in the same conditions as in Example 3, the aging treatment in an inert gas atmosphere, the final plastic working (cold-rolling (2-c), to a final sheet thickness of 0.15 mm), and then the low-temperature annealing, thereby manufacturing the copper alloy sheets (Sample Nos. 2-3 and 2-4), respectively.

Table 3

Ingot No.	Ni mass%	Si mass%	Mg mass%	Sn mass%	Zn mass%	Cr mass%	S mass%	Other elements mass%
2-Z	3.74	0.89	-	-	-	0.23	0.002	-
2-A	3.76	0.89	-	-	0.49	0.25	0.002	-
2-A-1	3.75	0.89	0.10	0.15	-	0.24	0.002	-
2-B	3.78	0.9	0.09	0.15	0.49	0.21	0.002	-
2-C	3.52	0.83	0.11	0.16	0.51	0.22	0.002	-
2-D	4.1	0.95	0.10	0.15	0.52	0.2	0.002	-
2-E	3.21	0.72	0.09	0.14	0.5	0.19	0.002	-
2-F	3.79	0.9	0.12	0.15	0.48	0.24	0.002	Ag:0.1
2-G	3.8	0.91	0.10	0.15	0.47	0.21	0.002	Co:0.31
2-H	3.81	0.92	0.08	0.17	0.51	0.2	0.002	Zr:0.17
2-I	3.76	0.89	0.10	0.15	0.5	0.25	0.002	Ti:0.16
2-J	3.76	0.91	0.09	0.14	0.5	0.6	0.002	-
2-K	5	1.17	0.11	0.21	0.49	0.23	0.002	-
2-L	3.78	0.88	0.08	0.16	1.7	0.21	0.002	-
2-M	3.81	0.92	0.38	0.20	0.5	0.2	0.002	-
2-N	3.74	0.87	0.08	2.01	0.48	0.19	0.002	-
2-O	3.76	0.9	0.12	0.17	0.52	0.1	0.002	-
2-PA	2.3	0.56	-	-	-	0.27	0.002	-
2-PB	2.3	0.56	0.10	-	-	0.27	0.002	-
2-PC	2.3	0.56	-	0.14	-	0.27	0.002	-
2-PD	2.3	0.56	-	-	0.51	0.27	0.002	-
2-PE	2.3	0.56	0.10	0.14	-	0.27	0.002	-
2-PF	2.3	0.56	0.10	-	0.51	0.27	0.002	-
2-PG	2.3	0.56	-	0.14	0.51	0.27	0.002	-
2-PH	2.3	0.56	0.10	0.14	0.51	0.27	0.002	-
2-Q	3.8	0.89	0.11	0.15	0.46	0.22	0.011	-
2-R	3.78	0.91	0.10	0.16	0.5	-	0.002	-
2-S	1.7	0.27	0.10	0.14	0.51	0.27	0.002	-

Note: The balance of each alloy was copper and unavoidable impurities; "-" not added.

The copper alloy sheets manufactured in Examples 3 and 4 each were tested and evaluated with respect to (1) crystal grain diameter, (2) crystal orientation, (3) bending property, (4) tensile strength, (5) electric conductivity, and (6) stress relaxation resistance.

(1) The crystal grain diameter (size) was measured according to JIS H 0501 (section method).

(2) The crystal orientations were determined by: irradiating the surface of the copper alloy sheet of a final product state (thickness 0.15 mm) with X-rays; and measuring intensities from the diffraction planes. Of those, the diffraction intensities of the {200}, {220}, and {311} planes were compared, to thereby obtain integration degrees of the crystal orientations (I{311}/(I{311}+I{220}+I{200})) and (I{311}×A/(I{311}+I{220}+I{200})). The conditions for the X-ray irradiation were: X-ray source CuKα1; tube voltage 40 kV; and tube current 20 mA.

(3) The bending property was evaluated based on a method described in JIS H 3110. A test piece with width 10 mm was bent at a load of 1,000 kgf. The test piece was cut out in a GW direction (with a bending axis perpendicular to the rolling direction) or a BW direction (with a bending axis parallel to the rolling direction). The bending property was evaluated with a ratio R/t, in which R represents a minimum bending radius at a limit of crack formation and t represents a thickness of the test piece.

(4) The tensile strength was determined according to JIS Z 2241, by using #5 test pieces described in JIS Z 2201.

(5) The electric conductivity was determined according to JIS H 0505.

(6) As an index of the stress relaxation resistance, was determined a stress relaxation ratio (S.R.R.), by applying a one-side holding block method of Electronics Materials Manufacturers Association of Japan Standard (EMAS-3003), in which the stress load was set so that the maximum surface stress would be 80% YS (80% yield strength, or 0.2% proof stress), and the resultant test piece was maintained in a constant temperature chamber at 150°C for 1,000 hours.

The results are shown in Table 4.

Table 4

	Ingot No	Sample No	Grain size μm	Value of expression (2)	Value of expression (3)	Bending property (R/t) GW	Bending property (R/t) BW	Tensile strength MPa	Electric conductivity %IACS	S.R.R. %
This invention	2-Z	2-0	5	0.10	0.50	1.0	1.0	850	38	9.3
	2-A	2-1	5	0.11	0.55	1.0	1.0	850	38	9.7
	2-A-1	2-1-1	5	0.12	0.60	1.0	1.0	850	38	9.5
	2-B	2-2	5	0.12	0.60	1.0	1.0	850	36	9.2
	2-B	2-3	5	0.09	0.45	1.5	1.5	890	36	8.9
	2-B	2-4	5	0.08	0.40	1.0	1.0	860	37	9.5
	2-C	2-5	5	0.10	0.50	1.0	1.0	830	38	9.2
	2-D	2-6	5	0.12	0.60	1.5	1.5	870	35	8.5
	2-E	2-7	5	0.11	0.55	1.0	1.0	810	39	9.2
	2-F	2-8	5	0.10	0.50	1.0	1.0	855	36	9.0
	2-G	2-9	5	0.11	0.55	1.0	1.0	860	35	9.5
	2-H	2-10	5	0.09	0.45	1.0	1.0	855	35	9.3
	2-I	2-11	5	0.10	0.50	1.0	1.0	850	36	9.6
	2-PA	2-23	5	0.11	0.51	0.5	0.75	732	40	10.2
	2-PB	2-24	5	0.1	0.55	0.5	0.75	731	39	10.4
	2-PC	2-25	5	0.09	0.52	0.5	0.5	730	38	9.9
	2-PD	2-26	5	0.11	0.51	0.75	0.5	729	39	10.4
	2-PE	2-27	5	0.1	0.52	0.75	0.75	721	38	10.1
	2-PF	2-28	5	0.12	0.5	0.5	0.5	712	39	9.9
	2-PG	2-29	5	0.13	0.52	0.75	0.5	734	38	9.5
	2-PH	2-30	10	0.13	1.3	1	1	720	37	9.7
Comparative Example	2-A	2-12	20	0.25	5.00	2.5	2.5	850	38	8.8
	2-B	2-13	20	0.23	4.60	2.5	2.5	855	37	8.2
	2-J	2-14	10	0.13	1.30	2.0	2.0	840	35	9.7
	2-K	2-15	Cracks during hot-working							
	2-L	2-16	5	0.13	0.65	1.5	1.5	845	30	9.4
	2-M	2-17	10	0.14	1.40	2.0	2.0	815	36	9.5
	2-N	2-18	Cracks during cold-working							
	2-O	2-19	10	0.21	2.10	2.5	2.5	820	37	9.7
	2-Q	2-20	Cracks during hot-working							
	2-R	2-21	15	0.20	3.00	2.5	2.5	840	37	9.8
	2-S	2-22	10	0.13	1.30	1.0	1.0	640	42	12.5

As is apparent from the results shown in Table 4, the sample Nos. 2-0 to 2-2, 2-1-1, and 2-5 to 2-11 (Example 3) and the sample Nos. 2-3 and 2-4 (Example 4) each had excellent characteristics satisfying all of a bending property (R/t) of less than 2, a tensile strength of 810 MPa or more, an electrical conductivity of 35%IACS or more, and a stress relaxation ratio of 10% or less. Further, the sample Nos. 2-23 to 2-30 had a slightly low tensile strength, and a slightly low stress relaxation ratio in some cases, but each had excellent properties satisfying both a bending property (R/t) of less than 2 and an electrical conductivity of 35% IACS or more.

Contrary to the above, the sample Nos. 2-12 and 2-13 (comparative examples) each had a value of the expression (2) or (3) falling outside of the ranges defined in the present invention, and had conspicuously poor bending property, which was presumably caused since the temperature of the solution treatment was too high.

The sample No. 2-14 (comparative example) was poor in bending property, due to a too large content of Cr.

The sample No. 2-15 (comparative example) could not be normally produced, since cracks were occurred during the hot-working, due to too large contents of Ni and Si.

The sample No. 2-16 (comparative example for the invention according to the above item [10]) was poor in electrical conductivity, due to a too high Zn content.

The sample No. 2-17 (comparative example for the invention according to the above item [11]) was excellent in stress relaxation resistance, but was conspicuously poor in bending property, due to a too high Mg content.

The sample No. 2-18 (comparative example for the invention according to the above item [12]) could not be produced normally, since cracks were occurred upon the cold-working, due to a too high Sn content.

The sample No. 2-19 (comparative example) was conspicuously poor in bending property, since the sample had a value of the expression (2) or (3) falling outside of the ranges defined in the present invention.

The sample No. 2-20 (comparative example) could not be normally produced, since cracks were occurred during the hot-working, due to the too large content of S.

The sample No. 2-21 (comparative example) was conspicuously poor in bending property, since the sample had a value of the expression (2) or (3) falling outside of the ranges defined in the present invention.

The sample No. 2-22 (comparative example) was conspicuously poor in mechanical strength and stress relaxation resistance, due to too small contents of Ni and Si.

INDUSTRIAL APPLICABILITY

The copper alloy of the present invention is preferable as a material to be used in terminal, connector and lead frame, as well as it is also preferable as a general-purpose conductive material, for example, for switch and relay.

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

CLAIMS

1. A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, and Si 0.3 to 1.0 mass%, with the balance being Cu and unavoidable impurities,

which satisfies expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

2. The copper alloy according to Claim 1, which further comprises at least one element selected from the group consisting of Zn 0.2 to 1.5 mass%, Mg 0.01 to 0.2 mass%, and Sn 0.05 to 1.5 mass%.

3. The copper alloy according to Claim 1, which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, and B 0.001 to 0.02 mass%, in a total content of 0.001 to 2.0 mass%.

4. A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, and S more than 0 and less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

5. The copper alloy according to Claim 4, which further comprises at least one element selected from the group consisting of Zn 0.2 to 1.5 mass%, Mg 0.01 to 0.2 mass%, and Sn 0.05 to 1.5 mass%.

6. The copper alloy according to Claim 4, which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, and B 0.001 to 0.02 mass%, in a total content of 0.001 to 2.0 mass%.

7. A copper alloy for electronic machinery and tools, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Mg 0.01 to 0.2 mass%, Sn 0.05 to 1.5 mass%, Zn 0.2 to 1.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies expression (1):

$$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5 \quad \cdots(1)$$

wherein, in expression (1), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size, and

which has good bending property.

8. The copper alloy according to Claim 7, which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, and B 0.001 to 0.02 mass%, in a total content of 0.001 to 2.0 mass%.

9. A copper alloy, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Cr 0.1 to 0.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies expression (2):

$$I\{311\} / (I\{311\} + I\{220\} + I\{200\}) < 0.15 \quad \cdots(2)$$

wherein, in expression (2), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; and I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface.

10. The copper alloy according to Claim 9, which further comprises at least one element selected from the group consisting of Zn 0.2 to 1.5 mass%, Mg 0.01 to 0.2 mass%, and Sn 0.05 to 1.5 mass%.

11. The copper alloy according to Claim 9, which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, Ti 0.005 to 0.3 mass%, Ag 0.005 to 0.3 mass%, and B 0.001 to 0.02 mass%.

12. A copper alloy, comprising Ni 2.0 to 4.5 mass%, Si 0.3 to 1.0 mass%, Cr 0.1 to 0.5 mass%, and S less than 0.005 mass%, with the balance being Cu and unavoidable impurities,

which satisfies expression (3):

$I\{311\} \times A / (I\{311\} + I\{220\} + I\{200\}) < 1.5$ ···(3)

wherein, in expression (3), I{311} represents an X-ray diffraction intensity from a {311} plane at a sheet surface; I{220} represents an X-ray diffraction intensity from a {220} plane at the sheet surface; I{200} represents an X-ray diffraction intensity from a {200} plane at the sheet surface; and A (μm) represents a crystalline grain size.

13. The copper alloy according to Claim 12, which further comprises at least one element selected from the group consisting of Zn 0.2 to 1.5 mass%, Mg 0.01 to 0.2 mass%, and Sn 0.05 to 1.5 mass%.

14. The copper alloy according to Claim 12, which further comprises at least one element selected from the group consisting of Zr 0.005 to 0.3 mass%, Co 0.05 to 2.0 mass%, Ti 0.005 to 0.3 mass%, Ag 0.005 to 0.3 mass%, and B 0.001 to 0.02 mass%.

INTERNATIONALSEARCHREPORT

International application No.
PCT/JP2005/010096

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.[7] C22C9/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.[7] C22C9/06

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 1971-2005
Registered utility model specifications of Japan 1996-2005
Published registered utility model applications of Japan 1994-2005

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus(JOIS)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-043731 A (KOBE STEEL CO., LTD.) 1999.02.16, claims, 【0016】【0017】 (No family)	1-14
X A	JP 11-256256 A (KOBE STEEL CO., LTD.) 1999.09.21, claims, 【0032】【0033】 (No family)	1-8 9-14
X A	JP 8-319527 A (KOBE STEEL CO., LTD.) 1996.12.03, claims, 【0019】【0025】【0031】 (No family)	1-6 7-14
A	US 2002/0108685 A1 (DOWA MINING CO., LTD.) 2002.08.15, claims, [0048],[0056] & JP 2002-180165 A	1-14
A	JP 2000-080428 A(KOBE STEEL CO., LTD.)2000.03.21, claims, 【0009】【0010】 (No family)	1-14

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-073130 A (KOBE STEEL CO., LTD.) 2000.03.07, claims, 【0009】【0010】 (No family)	1-14
A	US 6334915 B1 (KABUSHIKI KAISHA KOBE SEIKO SHO) 2002.01.01, claims, examples & JP 11-335756 A	1-14