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(54) Copper alloy sheet

(57) The present invention relates to a Cu-Ni-Sn-P-based copper alloy sheet having a specific composition, where the X-ray diffraction intensity ratio I(200)/I(220) in the sheet surface is set to be a given value or less and at the same time, anisotropy in the stress relaxation resistance characteristic is reduced by fining the grain size. The Cu-Ni-Sn-P-based copper alloy sheet of the present invention is excellent in the properties required for a terminal or connector and further satisfies the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy sheet. More specifically, the present invention relates to a copper alloy sheet having properties suitable for a connection component such as automotive terminal or connector.

BACKGROUND ART

[0002] A connection component such as automotive terminal or connector recently requires a performance enough to ensure reliability in a high-temperature environment such as engine room. One of most important properties for the reliability in a high-temperature environment is a contact-fitting force maintaining characteristic, that is, a stress relaxation resistance characteristic.

[0003] Fig. 4 shows a structure of a box-type connector (female terminal 3) representative of a connection component such as automotive terminal or connector. Fig. 4(a) is an elevational view and Fig. 4(b) is a cross-sectional view. In Fig. 4, the female terminal 3 has a pressing strip 5 cantilever-supported in an upper holder part 4 and when a male terminal (tab) 6 is inserted into the holder, the pressing strip 5 is elastically deformed and the male terminal (tab) 6 is fixed by the reaction force. Incidentally, in Fig. 4, 7 is a wire connecting part and 8 is an anchoring tongue strip.

[0004] As shown in Fig. 4, in the case where a stationary displacement is given to a spring-shaped component composed of a copper alloy sheet and a male terminal (tab) 6 is fitted at a spring-shaped contact part (pressing strip) 5, if the connector is kept standing in a high-temperature environment such as engine room, the contact-fitting force is lost with the lapse of time. Accordingly, the stress relaxation resistance characteristic is such a resistance characteristic against high temperatures as not allowing great reduction in the contact-fitting force of the spring-shaped component composed of a copper alloy sheet even when the connection component is kept standing in a high-temperature environment.

[0005] In the SAEJ (the Society of Automotive Engineers of Japan) Standards JASO-C400, as regards the stress relaxation resistance characteristic, the stress relaxation ratio after holding under the conditions of 150°C x 1,000 hr is specified to be 15% or less. Figs. 3(a) and (b) each shows a tester for the stress relaxation resistance characteristic according to this standard. Using this tester, a test specimen 1 cut out into a strip shape is fixed at one end to a rigid test board 2, warped by lifting another end in a cantilever manner (d: warpage size), kept standing at a predetermined temperature for a predetermined time, and then unloaded at room temperature, and the warpage size after unloading (permanent distortion) is determined as δ. Here, the stress relaxation ratio (RS) is represented by $RS = (\delta/d) \times 100$.

[0006] However, the stress relaxation ratio of a copper alloy sheet has anisotropy and takes a different value according to the direction in which the longitudinal direction of the test specimen runs with respect to the rolling direction of the copper alloy sheet. In this respect, the connection component such as automotive terminal or connector must have a stress relaxation ratio of 15% or less in the direction used as a spring, that is, in either one direction parallel or orthogonal to the rolling direction of the sheet.

[0007] As for the copper alloy excellent in the stress relaxation resistance characteristic, a Cu-Ni-Si-based alloy, a Cu-Ti-based alloy, a Cu-Be-based alloy and the like have been heretofore widely known, but in recent years, a Cu-Ni-Sn-P-based alloy having a relatively small additive element content has been used. This Cu-Ni-Sn-P-based alloy allows for ingot making in a shaft furnace which is a large-scale melting furnace with the opening being widely opened to the atmosphere, and because of its high productivity, a great cost down can be achieved.

[0008] Also, various techniques for enhancing the stress relaxation resistance characteristic of the Cu-Ni-Sn-P-based alloy itself have been conventionally proposed. For example, Patent Documents 1 and 2 disclose a technique of uniformly and finely dispersing an Ni-P intermetallic compound in a Cu-Ni-Sn-P-based alloy matrix to enhance the electrical conductivity and at the same time, enhance the stress relaxation resistance characteristic and the like, and Patent Documents 2 and 3 disclose a technique of decreasing the P content of a Cu-Ni-Sn-P-based alloy to obtain a solid solution-type copper alloy reduced in the precipitation of an Ni-P compound. Furthermore, Patent Documents 4 and 5 disclose a technique of specifying the substantial temperature and holding time in finish annealing at the production of a Cu-Ni-Sn-P-based alloy sheet to enhance the electrical conductivity and at the same time, enhance the stress relaxation resistance characteristic and the like.

Patent Document 1: Japanese Patent No. 2,844,120
Patent Document 2: Japanese Patent No. 3,871,064
Patent Document 3: JP-A-11-293367 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")
Patent Document 4: JP-A-2002-294368
Patent Document 5: JP-A-2006-213999

DISCLOSURE OF THE INVENTION

[0009] Problems that the Invention is to Solve

[0010] However, mechanical properties of these conventional Cu-Ni-Sn-P-based alloys enhanced in the stress relaxation resistance characteristic are such that, for example, when the 0.2%-proof stress is about 500 MPa, the elongation is only less than 10%, and the elongation is low for the strength. Also, as for the terminal/connector properties, while a stress relaxation ratio of 15% or less is achieved in the direction parallel to the rolling direction, the electrical conductivity is as low as less than 35% IACS.

[0011] Heretofore, however, press forming such as bending of a Cu-Ni-Sn-P-based alloy sheet which becomes a raw material of the connection component such as automotive terminal or connector is mostly performed under working conditions in a relatively low-speed deformation region where the sheet is less subject to a large strain rate. As a result, even when elongation of the conventional Cu-Ni-Sn-P-based alloy is low as described above, generation of various shaping defects such as cracking can be suppressed by virtue of, for example, mild or devised working conditions and there are not caused many troubles in the working into a terminal or a connector.

[0012] Meanwhile, the process of press-forming a copper alloy sheet and producing a connection component such as automotive terminal or connector shown in Fig. 4 recently has also become higher and higher in the efficiency and speed. In such high-efficiency and high-speed press forming, during bending work such as 180° contact bending or 90° bending after notching, the sheet is irresistibly subject to a large strain rate and under working conditions in a high-speed deformation region with such a large strain rate, various shaping defects such as cracking are readily generated. To avoid this problem, high formability, that is, a higher elongation value, is required for the raw material copper alloy sheet.

[0013] However, there is a high possibility that conventional Cu-Ni-Sn-P-based alloys with low elongation cannot cope with the high-efficiency high-speed press forming to thereby cause various shaping defects such as cracking. This generation of shaping defects not only reduces the yield of the shaped article but also could be a serious problem in the production line, such that the high-efficiency high-speed press forming process (line) is stopped on every occurrence of a shaping defect.

[0014] Conventional Cu-Ni-Sn-P-based alloys have low elongation as described above or techniques for enhancing the elongation characteristic itself are not found, and therefore, the number of cases disclosing the elongation value itself is few. In this respect, the elongation value is exceptionally disclosed in Examples (Tables) of Japanese Patent No. 3,871,064 and JP-A-2002-294368. In Japanese Patent No. 3,871,064, taking a most excellent example with an elongation of 10.1%, the 0.2%-proof stress as the mechanical properties is 521 MPa, the stress relaxation ratio is 12.7% in the direction parallel to the rolling direction, and the electrical conductivity is 31.2% IACS. In JP-A-2002-294368, taking a most excellent example with an elongation of 9.1%, the 0.2%-proof stress as the mechanical properties is 530 MPa, the stress relaxation ratio is 9.8% in the direction parallel to the rolling direction, and the electrical conductivity is 33.2% IACS.

[0015] Accordingly, it is corroborated by these Japanese Patent No. 3,871,064 and JP-A-2002-294368 that, as described above, in conventional Cu-Ni-Sn-P-based alloys, when the 0.2%-proof stress is about 500 MPa, the elongation is less than 10% and not high for the strength and also, despite a stress relaxation ratio of 15% or less, the electrical conductivity is not high.

[0016] To cope with this, a Cu-Ni-Sn-P-based alloy sheet having a higher elongation value responsive to the above-described high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector is demanded. Moreover, this copper alloy sheet needs to satisfy not only elongation but also other properties required for a connection component such as automotive terminal or connector.

[0017] That is, there is demanded a Cu-Ni-Sn-P-based alloy sheet having, as terminal/connector properties, an electrical conductivity of 32% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further having, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and an elongation of 10% or more.

[0018] In view of these points, a first object of the present invention is to provide a Cu-Ni-Sn-P-based alloy sheet with excellent strength-ductility balance, which is responsive to the above-described high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and also satisfies the properties required for a terminal or connector.

[0019] Meanwhile, the stress relaxation ratio of a rolled copper alloy sheet (obtained by rolling) has anisotropy and takes a different value according to the direction in which the longitudinal direction of the female terminal 3 in Fig. 4 runs with respect to the rolling direction of the raw material copper alloy sheet. The same applies to the measurement of the stress relaxation ratio, and the measured stress relaxation ratio takes a different value according to the direction in which the longitudinal direction of a test specimen runs with respect to the rolling direction of the raw material copper alloy sheet. Accordingly, the stress relaxation ratio is liable to be low in the orthogonal direction than in the parallel direction with respect to the rolling direction of the copper alloy sheet.

[0020] In this respect, at the time of press working a raw material copper alloy sheet to produce a female terminal 3 in Fig. 4, blanking is sometimes performed such that the longitudinal direction of the female terminal 3 (the longitudinal direction of the pressing strip 5) runs in the direction orthogonal to the rolling direction. A high stress relaxation resistance characteristic is usually required for the bending (elastic deformation) in the length direction of the pressing strip 5. Accordingly, when blanking is performed to allow for running in the direction orthogonal to the rolling direction, it is required to have a high stress relaxation resistance characteristic not in the parallel direction but in the orthogonal direction with respect to the rolling direction of the copper alloy sheet.

[0021] In this respect, when the stress relaxation ratio is high in the direction orthogonal to the rolling direction as well as in the direction parallel to the rolling direction, even when the blanking is performed in either one direction of parallel direction and orthogonal direction with respect to the rolling direction, the stress relaxation resistance characteristic as a terminal or connector can be satisfied irrespective of the blanking direction of the raw material copper alloy sheet.

[0022] In view of this point, a second object of the present invention is to provide a Cu-Ni-Sn-P-based copper alloy sheet with an excellent stress relaxation resistance characteristic, which satisfies, as a terminal or connector, a high stress relaxation ratio in the direction orthogonal to the rolling direction as well as in the direction parallel to the rolling direction.

[0023] On the other hand, the conventional Cu-Ni-Sn-P-based copper alloy enhanced in the stress relaxation resistance characteristic is not excellent in bendability or press punchability. The working of a copper alloy sheet into a terminal or connector sometimes involves a severe bending work such as contact bending or 90° bending after notching or a stamping work such as press punching of the sheet, and bendability high enough to withstand such a working or excellent press punchability is becoming required.

[0024] However, like conventional Cu-Ni-Sn-P-based alloy enhanced in the stress relaxation resistance characteristic, when the strength is increased, for example, to a 0.2%-proof stress of 500 MPa or more by adding a solid solution strengthening element or increasing the working ratio of cold rolling, deterioration of bendability is inevitably incurred and it is quite difficult to satisfy both of required strength and bendability.

[0025] Also, although the usage or alloy system is utterly different, in other copper alloys such as Cu-Fe-P-based copper alloy sheet for use as a lead frame, a technique of controlling the chemical components, for example, adding a small amount of Pb, Ca or the like or dispersing a compound working out to a starting point of fracture, or a technique of controlling a grain size, has been heretofore generally employed as the means for enhancing the press punchability. However, when such a technique is intended to be applied to a Cu-Ni-Sn-P-based copper alloy, there may arise a problem that the control itself is difficult or other properties are deteriorated or that the production cost in turn rises.

[0026] In the field of Cu-Fe-P-based copper alloy sheet, many proposals have been made to enhance the press punchability or bendability by taking note of the sheet texture (see, JP-A-2000-328158, JP-A-2002-339028, JP-A-2000-328157 and JP-A-2006-63431). In these techniques, the press punchability is enhanced mainly by controlling the accumulation degree of crystal orientation of the copper alloy sheet.

[0027] However, in a Cu-Ni-Sn-P-based copper alloy sheet greatly differing in the alloy system or properties from the Cu-Fe-P system, there have not heretofore been made many proposals on this technique of enhancing the press punchability. The reason therefor is presumed because necessity for or usage requiring enhancement of press punchability of the Cu-Ni-Sn-P-based copper alloy sheet has not conventionally been so pressing.

[0028] In view of these points, a third object of the present invention is to provide a Cu-Ni-Sn-P-based copper alloy sheet satisfying, as a terminal or connector, the requisite properties such as stress relaxation resistance characteristic and bendability, and a fourth object of the present invention is to provide a Cu-Ni-Sn-P-based copper alloy sheet which not only satisfies the properties required for a terminal or connector, such as stress relaxation resistance characteristic, but also is excellent in the press punchability.

Means for Solving the Problems

[0029] In order to achieve the first object of the present invention, the gist of the copper alloy sheet with excellent strength-ductility balance (hereinafter sometimes referred to as a first embodiment of the present invention) is a copper alloy sheet comprising, in terms of mass%, 0.1 to 3.0% of Ni, 0.01 to 3.0% of Sn and 0.01 to 0.3% ofP, with the balance being copper and inevitable impurities, wherein the copper alloy sheet has, as terminal/connector properties, an electrical conductivity of 32% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further has, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and an elongation of 10% or more.

[0030] Another gist of the first embodiment of the present invention is a copper alloy sheet comprising, in terms of mass%, 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% of P, with the balance being copper and inevitable impurities, wherein the copper alloy sheet has an intensity peak at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern, and wherein the copper alloy sheet has, as terminal/connector properties, an electrical conductivity of 32% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further has, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and an elongation of 10% or more.

[0031] As regards preferred properties, the copper alloy sheet has, as terminal/connector properties, an electrical conductivity or 35% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further has, as mechanical properties, a 0.2%-proof stress of 520 MPa or more and an elongation of 12% or more.

[0032] This copper alloy sheet preferably further comprises at least one member selected from the group consisting of, in terms of mass%, 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. Also, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, in a total amount of 1.0 mass% or less. Furthermore, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, in a total amount of 0.1 mass% or less.

[0033] The method for producing any one of copper alloy sheets described above or later according to the first embodiment of the present invention comprises casting a copper alloy having any one of compositions described above or later and subjecting the copper alloy ingot to hot rolling, cold rolling and finish annealing in this order to obtain a copper alloy sheet, wherein the finish annealing is performed at a maximum peak temperature of the copper alloy sheet of 500 to 800°C and the average temperature rise rate of the copper alloy sheet to the temperature above is 50°C/s or more, and wherein when cooling the copper alloy sheet to room temperature, the average cooling rate of the copper alloy sheet from 400°C to room temperature is from 40 to 100°C/h, whereby the copper alloy sheet thus obtained has an intensity peak between 100° and 102° of the X-ray diffraction angle (2θ) in the X-ray diffraction pattern, and has, as terminal properties, an electrical conductivity of 32% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further has, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and an elongation of 10% or more.

[0034] In order to achieve the second object of the present invention, the gist of the copper alloy sheet with excellent stress relaxation resistance characteristic (hereinafter sometimes referred to as a second embodiment of the present invention) is a copper alloy sheet comprising, in terms of mass%, 0.1 1 to 3.0% of Ni, 0.01 to 3.0% of Sn and 0.01 to 0.3% ofP, with the balance being copper and inevitable impurities, wherein the copper alloy sheet has a ratio I(200)/I(220) of a X-ray diffraction intensity I(200) from (200) plane in the sheet surface to a X-ray diffraction intensity I(220) from (220) plane in the sheet surface of 0.25 or less, and has an average grain size of 5.0 μm or less.

[0035] This copper alloy sheet preferably further comprises at least one member selected from the group consisting of, in terms of mass%, 0.5% or less of Fe, 1% or less ofZn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. Also, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, in a total amount of 1.0 mass% or less. Furthermore, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, in a total amount of 0.1 mass% or less.

[0036] In order to achieve the third object of the present invention, the gist of the copper alloy sheet excellent in the stress relaxation resistance characteristic and bendability (hereinafter sometimes referred to as a third embodiment of the present invention) is a copper alloy sheet comprising, in terms of mass%, 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% ofP, with the balance being copper and inevitable impurities, wherein the copper alloy sheet has a texture in which a distribution density of Brass orientation is 40% or less and a sum of distribution densities of Brass orientation, S orientation and Copper orientation is 30 to 90%.

[0037] This copper alloy sheet preferably further comprises at least one member selected from the group consisting of, in terms of mass%, 0.5% or less of Fe, 1% or less of Zn, 0.1% or less ofMn, 0.1% or less of Si and 0.3% or less of Mg. Also, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, in a total amount of 1.0 mass% or less. Furthermore, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, in a total amount of 0.1 mass% or less.

[0038] In order to achieve the fourth object of the present invention, the gist of the copper alloy sheet excellent in the stress relaxation resistance characteristic and press punchability (hereinafter sometimes referred to as a fourth embodiment of the present invention) is a copper alloy sheet comprising, in terms of mass%, 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% ofP, with the balance being copper and inevitable impurities, wherein a value obtained by dividing a half-value breadth of a X-ray diffraction intensity peak from {200} plane in the sheet surface by a height of the peak is 1.0×10^{-4} or more.

[0039] This copper alloy sheet preferably further comprises at least one member selected from the group consisting of, in terms of mass%, 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. Also, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, in a total amount of 1.0 mass% or less. Furthermore, the copper alloy sheet preferably further comprises at least one member selected from the group consisting of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, in a total amount of 0.1 mass% or less.

Advantage of the Invention

(Effects of First Embodiment of the Present Invention)

[0040] The present inventors have succeeded in obtaining a copper alloy sheet with excellent strength-ductility balance according to the first embodiment of the present invention by the above-described characteristic control of finish annealing conditions, where the electrical conductivity is enhanced more than the usually expected effect of elevating the electrical conductivity without reducing the strength which usually decreases by the finish annealing and the elongation of the obtained copper alloy sheet is enhanced while maintaining the stress relaxation resistance characteristic. From a commonsense standpoint, the strength after finish annealing usually decreases due to a recovery/recrystallization phenomenon during finish annealing. Nevertheless, under the above-described characteristic control of finish annealing conditions, surprisingly, the strength is not reduced but is maintained and the elongation is rather enhanced. The electrical conductivity is also elevated.

[0041] Namely, in the conventional Cu-Ni-Sn-P-based alloy sheet, the elongation is less than 10% despite a 0.2%-proof stress of 500 MPa or more, and the electrical conductivity is less than 35% IACS despite a stress relaxation ratio of 15% or less. On the other hand, according to the first embodiment of the present invention, a novel Cu-Ni-Sn-P-based alloy sheet having, even when the 0.2%-proof stress is 500 MPa or more, an elongation of 10% or more, an electrical conductivity of 32% IACS or more and a stress relaxation ratio of 15% or less is obtained. More excellent properties of this Cu-Ni-Sn-P-based alloy sheet are such that the electrical conductivity is 35% IACS or more, the stress relaxation ratio is 15% or less in the direction parallel to the rolling direction, the 0.2%-proof stress is 520 MPa or more, and the elongation is 12% or more.

[0042] This copper alloy sheet with excellent strength-ductility balance according to the first embodiment of the present invention was subjected to systematic analysis and analyzed in detail for the grain shape, analyzable fine crystallized product such as Ni-P compound, the oxide and the like, but to date, a systematic clear distinction in terms of the structure cannot be drawn between the conventional copper alloy sheet and the present invention. The systematic analysis instruments used herein are SEM (scanning electron microscope), TEM (transmission electron microscope) and the like, which are generally used for direct systematic analysis of this type. Of course, the copper alloy sheet compositions investigated are utterly the same Cu-Ni-Sn-P-based alloy and the production conditions are the same conditions except for changing the finish annealing conditions among samples.

[0043] Therefore, the present inventors further performed, as the systematic analysis, X-ray diffraction which is special as compared with the direct systematic analysis means, that is, SEM and TEM. As a result, it has been found that, as described later, in the copper alloy sheet with excellent strength-ductility balance according to the first embodiment of the present invention, an intensity peak is present at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern, whereas in the conventional Cu-Ni-Sn-P-based alloy sheet, such an intensity peak is not present.

[0044] In other words, the present inventors have found that when such an intensity peak is present in a Cu-Ni-Sn-P-based alloy sheet, even with a 0.2%-proof stress of 500 MPa or more, the elongation is 10% or more, the electrical conductivity is 32% IACS or more, and the stress relaxation ratio is 15% or less. The present inventors have also found that when such an intensity peak is not present, like the conventional Cu-Ni-Sn-P-based alloy sheet, the elongation is less than 10% despite a 0.2%-proof stress of 500 MPa or more and the electrical conductivity is less than 32% IACS despite a stress relaxation ratio of 15% or less. That is, in fact, whether or not the alloy sheet is a novel Cu-Ni-Sn-P-based alloy sheet satisfying all of 0.2%-proof stress, elongation, electrical conductivity and stress relaxation resistance characteristic is depending on whether the above-described specific intensity peak is present or not.

[0045] The presence of the specific intensity peak, namely, the specific intensity peak at the X-ray diffraction angle (2θ) between 100° and 102°, means that a certain compound is present in the copper alloy sheet texture. The present inventors anticipate that, as described later, this compound is a specific Sn-based compound. However, also as described later, despite various analyses on the relationship between the possible intermetallic compound in this alloy system and the intensity peak position in the X-ray diffraction pattern, what intermetallic compound assumes the above-described specific intensity peak is not clearly known and at present, the anticipation above is only a matter of speculation. Accordingly, how or whether the specific intensity peak contributes to the above-described difference or enhancement in terms of the properties of the Cu-Ni-Sn-P-based alloy sheet is not necessarily clarified.

[0046] In this way, although the specific intensity peak above is an important measure of novelty of the copper alloy sheet with excellent strength-ductility balance according to the first embodiment of the present invention, it is not always clear whether the specific intensity peak is an essential requirement to bring out the above-described difference in the properties.

[0047] However, according to the first embodiment of the present invention, a Cu-Ni-Sn-P-based alloy sheet with excellent strength-ductility balance, which is responsive to the above-described high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies also the properties required for a terminal or connector, can be provided.

(Effects of Second Embodiment of the Present Invention)

[0048] In the second embodiment of the present invention, the X-ray diffraction intensity ratio I(200)/I(220) is specified so as to suppress the development of Cube orientation of the Cu-Ni-Sn-P-based copper alloy sheet and develop a specific crystal orientation except for the Cube orientation. In combination with this, the average grain size is specified to be fine as 5.0 μm or less. By virtue of these constructions, in the second embodiment of the present invention, anisotropy in specific directions such as parallel direction or orthogonal direction with respect to the rolling direction is reduced, whereby the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction is enhanced and at the same time, the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction is made small.

[0049] Contrary to the second embodiment of the present invention, if the Cube orientation is developed, if the development of a specific crystal orientation except for the Cube orientation is suppressed or if the average grain size is coarsened, anisotropy in a specific direction such as parallel direction with respect to the rolling direction is intensified in any case and the stress relaxation resistance characteristic in the orthogonal direction is rather not enhanced. Also, the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction cannot be made small and anisotropy (difference in the stress relaxation resistance characteristic) between these two directions becomes large.

(Effect of Third Embodiment of the Present Invention)

[0050] In the case of a normal copper alloy sheet, mainly the following Cube orientation, Goss orientation, Brass orientation (hereinafter sometimes referred to as B orientation), Copper orientation (hereinafter sometimes referred to as Cu orientation), S orientation and the like form a texture, and crystal planes corresponding to these orientations are present.

[0051] The formation of this texture differs according to the working or heat-treatment method even in the same crystal system. The texture of a sheet material obtained by rolling is indicated by the rolling plane and rolling direction. The rolling plane is expressed by {ABC}, and the rolling direction is expressed by <DEF>. Based on these expressions, each orientation is expressed as follows.

Cube orientation	{001}<100>
Goss orientation	{011}<100>
Rotated-Goss orientation	{011}<011>
Brass orientation (B orientation)	{011}<211>
Copper orientation (Cu orientation)	{112}<111>
	(or D orientation {44 11}<11 11 8>)
S orientation	{123}<634>
B/G orientation	{011}<511>
B/S orientation	{168}<211>
P orientation	{011}<111>

[0052] As described above, the texture of a normal copper alloy sheet is composed of a fairly large number of orientation factors and when the constituent ratio of these factors is varied, the plastic anisotropy of the sheet material changes. In the case of a Cu-Ni-Sn-P-based copper alloy sheet, the properties such as stress relaxation resistance characteristic and bendability are greatly changed.

[0053] According to the knowledge of the present inventors, for enhancing the bendability of a Cu-Ni-Sn-P-based copper alloy sheet while maintaining the high strength, the distribution density of Brass orientation (B orientation) needs to be reduced. In addition, for achieving a good balance between high density and bendability, the sum of distribution densities of B orientation, S orientation and Cu orientation also needs to be controlled to a specific range.

[0054] Although the alloy system differs, there is conventionally a case, for example, where, in a Cu-Fe-P-based copper alloy sheet, the orientation density of Cube orientation [hereinafter sometimes referred to as D(Cube)] is controlled to an appropriate range with an attempt to enhance and stabilize the bendability. However, according to the knowledge of the present inventors, such control of the Cube orientation cannot enhance the bendability particularly of a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, which is enhanced in the stress relaxation resistance characteristic.

[0055] In a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, out of the texture above, particularly the distribution density ofB orientation and further the distribution densities ofB orientation, S orientation and Cu orientation have great effect on the strength. As the distribution densities ofB orientation, S orientation and Cu orientation are larger, the rolled texture is developed and the strength is higher.

[0056] However, on the other hand, as the distribution density of B orientation is larger or the sum of distribution densities of B orientation, S orientation and Cu orientation is larger, conversely, the stress relaxation resistance characteristic or bendability decreases. In contrast, as the distribution density of B orientation is smaller or the sum of distribution densities of B orientation, S orientation and Cu orientation is smaller, the crystal orientations become random and the stress relaxation resistance characteristic or bendability is enhanced.

[0057] That is, in a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, for enhancing the stress relaxation resistance characteristic and bendability while maintaining the high strength, it is effective to reduce the distribution density ofB orientation and simultaneously control the sum of distribution densities ofB orientation, S orientation and Cu orientation to a specific range.

(Effect of Fourth Embodiment of the Present Invention)

[0058] In the fourth embodiment of the present invention, the dislocation density of the Cu-Ni-Sn-P-based copper alloy sheet texture is controlled. More specifically, the dislocation density of the Cu-Ni-Sn-P-based copper alloy sheet texture is increased, whereby the press punchability is enhanced. According to the knowledge of the present inventors, as for the dislocation density, the amount of dislocations introduced can be controlled by the rolling conditions of the Cu-Ni-Sn-P-based copper alloy and at the same time, this control of the dislocation density has a great effect of enhancing the press punchability.

[0059] In the fourth embodiment of the present invention, it is not intended to control the crystal orientation texture such as accumulation ratio of a specific orientation (crystal orientation) by specifying the X-ray diffraction intensity from a specific crystal orientation in a sheet surface of a Cu-F-P-based copper alloy or the like, which is attempted, for example, in JP-A-2000-328158, JP-A-2002-339028, JP-A-2000-328157 and JP-A-2006-63431. In a copper alloy originally having random orientations, there is a large limitation in increasing only the accumulation ratio of a specific orientation. This applies also to the case of controlling the texture such as accumulation ratio of a specific orientation (crystal orientation) described, for example, in JP-A-2000-328158, JP-A-2002-339028, JP-A-2000-328157 and JP-A-2006-63431. In other words, the conventional control of the texture has a large limitation in terms of the effect of enhancing the press punchability, not only in a Cu-Fe-P-based copper alloy sheet but also in a Cu-Ni-Sn-P-based copper alloy sheet.

[0060] The dislocation density which is controlled in the fourth embodiment of the present invention is an extremely microscopic issue and it is very difficult to directly observe or quantify the dislocation density introduced into the Cu-Ni-Sn-P-based copper alloy sheet texture. However, according to the knowledge of the present inventors, the dislocation density introduced into the Cu-Ni-Sn-P-based copper alloy sheet texture is fairly well correlated to the half-value breadth of the X-ray diffraction intensity peak, particularly, the value obtained by dividing the half-value breadth by the height of the X-ray diffraction intensity peak.

[0061] In this case, the dislocation density is correlated equally to any X-ray diffraction intensity peak. However, the X-ray diffraction intensity peak from {200} plane in the sheet surface, specified in the fourth embodiment of the present invention, is not large (high) as the X-ray diffraction intensity peak which should divide the half-value breadth, in comparison with X-ray diffraction intensities from other planes, and because of a relatively fair half-value breadth, the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak by the height is highly reliable. Accordingly, in the fourth embodiment of the present invention, the dislocation density is indirectly but exactly and reproducibly specified and quantified by the X-ray diffraction intensity peak from {200} plane in the sheet surface.

[0062] In this way, in the fourth embodiment of the present invention, the amount of dislocation density is specified by the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface, which is closely correlated to the amount of dislocation density, to enhance the press punchability and satisfy the press punchability required for the Cu-Ni-Sn-P-based copper alloy sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

[0063]

Fig. 1 shows an explanatory view showing the X-ray diffraction pattern of a copper alloy sheet.
Fig. 2 shows an explanatory view showing the X-ray diffraction pattern of a copper alloy sheet.
Fig. 3 shows cross-sectional views for explaining the stress relaxation resistance test of a copper alloy sheet.
Fig. 4 shows cross-sectional views showing the structure of a box-type connector.
Fig. 5 shows a schematic view showing the half-value breadth of the X-ray diffraction intensity peak.
Fig. 6 shows explanatory views showing the measuring method of a shear plane ratio.

Description of Reference Numerals and Signs

[0064]

a: Specific intensity peak between 100° and 102° in the X-ray diffraction pattern
1: test specimen
2: test board
3: box-type connector (female terminal)
4: upper holder part
5: pressing strip
6: male terminal
7: wire connecting part
8: anchoring tongue strip

BEST MODE FOR CARRYING OUT THE INVENTION

[0065] The present invention is described in detail below. In the context of the present invention, all percentages defined by the mass are the same as those defined by the weight, respectively.

(1) Best Mode for Carrying Out First Embodiment of the Present Invention

[0066] The first embodiment of the present invention is described in detail below.

(X-Ray Diffraction)

[0067] In the first embodiment of the present invention, a specific intensity peak in the X-ray diffraction pattern is specified as an important measure of novelty of a copper alloy sheet with excellent strength-ductility balance. That is, in the X-ray diffraction pattern of the copper alloy sheet, an intensity peak is specified to be present at the X-ray diffraction angle (2θ) between 100° and 102°.

[0068] This specific intensity peak is, as described later, presumed to be assignable to an Ni-Sn-based compound, but because of an alloy component or alloy element, the peak height is extremely low as compared with the intensity peak height of Cu which is originally main as the matrix. Whether the degree of this specific peak height contributes to the difference in the properties such as elongation of the Cu-Ni-Sn-P-based alloy sheet is not clearly known as described above. However, also as described above, the properties of the copper alloy sheet can be clearly distinguished from conventional properties of low elongation and low electrical conductivity by whether or not this specific intensity peak is present.

[0069] Accordingly, in the first embodiment of the present invention, when it is objectively recognized that an intensity peak rising over fluctuation (variation) of the intensity peak due to noise is substantially present at the X-ray diffraction angle (2θ) between 100° and 102° (in the vicinity of 101 °) in the X-ray diffraction pattern, it is specified that the specific intensity peak is present.

(Figs. 1 and 2)

[0070] Fig. 1 shows X-ray diffraction patterns of various copper alloy sheets of Inventive Example 1 and Comparative Examples 20, 22 and 23 in Table 2 in First Example described below, and Fig. 2 shows only the X-ray diffraction pattern of Inventive Example 1 extracted from Fig. 1.

[0071] In both of Figs. 1 and 2, the ordinate indicates the X-ray diffraction intensity (CPS) and the abscissa indicates the X-ray diffraction angle (2θ). The X-ray diffraction intensity on the ordinate differs in the range and is from 0 to 1,000 CPS in Fig. 1 and from 0 to 3,500 CPS in Fig. 2. The X-ray diffraction angle also differs in the range and is from 30 to 112° in Fig. 1 and from 80 to 120° in Fig. 2.

[0072] In Fig. 1; the top X-ray diffraction pattern is Inventive Example 1, and X-ray diffraction patterns of Comparative Examples 20, 22 and 23 are arranged in this order from the upper side. For the sake of showing these patterns together in the same Fig. 1, each reference line except for Comparative Example 23 is arranged by daringly raising the bank.

[0073] In Fig. 1, the X-ray diffraction patterns of various copper alloy sheets of Inventive Example 1 and Comparative Examples have an intensity peak of the main Cu, as shown by the arrow Cu, appearing in the portion of the same X-ray diffraction angle (2θ), because these copper alloys are in the same composition system. The intensity peak position is present between 50° and 51°, between 59° and 60°, between 89° and 90°, and between 110° and 111°, of the X-ray diffraction angle.

[0074] In Fig. 1, the X-ray diffraction pattern of Inventive Example 1 and the X-ray diffraction pattern of each Comparative Example differ only in the point whether or not the specific intensity peak denoted by the arrow a is present at the X-ray diffraction angle (2θ) between 100° and 102°. In Fig. 1 and Fig. 2 extracting only Inventive Example 1, it is objectively recognized only in Inventive Example 1 that an intensity peak rising over fluctuation (variation) due to noise is substantially present.

(Compound Implied by Intensity Peak)

[0075] Usually, a compound (precipitate) having such an intensity peak a (specific peak) appearing at the X-ray diffraction angle (2θ) between 100° and 102° is itself unknown in the Cu-Ni-Sn-P-based alloy. The compound having a closest X-ray diffraction angle is an Ni_3Sn compound (precipitate) oriented in (511) plane. The X-ray diffraction angle of this compound is 102°, and an intensity peak appears at the 102° position. However, this X-ray diffraction angle (2θ) is not between 100° and 102° specified in the first embodiment of the present invention, and the intensity peak position is slightly shifted to the higher angle side.

[0076] Incidentally, in Fig. 2, intensity peak positions (X-ray diffraction angles) of other main compounds (precipitates) produced in the Cu-Ni-Sn-P-based alloy are also shown, confirming that the compound (precipitate) of which intensity peak position appears between 100° and 102° is itself unknown. In Fig. 2, the Ni_3Sn compound oriented in (331) plane and the Cu_3Sn compound oriented in (420) plane have an intensity peak position between 81° and 82°. The intensity peak position of the Ni_3Sn compound oriented in (420) plane is in the vicinity of 84°, the intensity peak position of the Cu_3Sn compound oriented in (422) plane is between 91° and 92°, the intensity peak position of the Ni_3Sn compound oriented in (422) plane is in the vicinity of 94°, the intensity peak position of the Cu_3Sn compound oriented in (511) plane is in the vicinity of 99°, the intensity peak position of the Cu_3Sn compound oriented in (440) plane is between 111° and 112°, the intensity peak of the Ni_3Sn compound oriented in (440) plane is between 115° and 116°, and the intensity peak position of the Cu_3Sn compound oriented in (531) plane is in the vicinity of 120°.

[0077] Accordingly, the reasonable presumption based on these facts is that the intensity peak position of the compound (precipitate) having the above-described specific intensity peak a, specified in the first embodiment of the present invention, is shifted to the lower angle side and appears between 100° and 102° because a part ofNi in the Ni_3Sn compound (precipitate) is replaced by Cu. That is, the compound (precipitate) of which the X-ray diffraction angle (2θ) appears between 100° and 102° (specific intensity peak a), specified in the first embodiment of the present invention, is considered to be an Sn-based compound containing Ni and Cu resulting from replacement of a part ofNi by Cu (hereinafter sometimes referred to as a specific Sn-based compound). However, as described above, it is not always clear whether the "compound" considered to be this Sn-based compound containing Ni and Cu contributes to the above-described difference in the properties such as elongation of the Cu-Ni-Sn-P-based alloy sheet.

[0078] Nevertheless, in fact, the Cu-Ni-Sn-P-based alloy sheet of which intensity peak is present at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern of the copper alloy sheet is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector, is excellent in the stress relaxation resistance characteristic and electrical conductivity as a terminal or connector, and has excellent strength-ductility balance. Accordingly, in the following, the component composition and production method are described on the presumption that the specific intensity peak a in the X-ray diffraction pattern is assignable to the above-described specific Sn-based compound.

(Copper Alloy Component Composition)

[0079] The component composition of the copper alloy according to the first embodiment of the present invention is described below. In the first embodiment of the present invention, as a premise, the component composition of the copper alloy is, as described above, a Cu-Ni-Sn-P-based alloy allowing for ingot making in a shaft furnace and because of its high productivity, enabling a great cost down.

[0080] In order to obtain a copper alloy that is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies the properties required for a connection component such as automotive terminal or connector and also that is assured of excellent strength-ductility balance and at the same time, excellent in the stress relaxation resistance characteristic and electrical conductivity, the copper alloy fundamentally comprises 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% of P, with the balance being copper and inevitable impurities. The % indicative of the content of each element means mass%. The alloy elements of the copper alloy are described below by referring to the reasons of addition or restraint.

(Ni)

[0081] Ni is an element necessary for enhancing the strength or stress relaxation resistance characteristic by forming a fine precipitate with P. Also, Ni forms the specific Sn-based compound related to the specific intensity peak in the X-ray diffraction pattern specified in the first embodiment of the present invention. A content of less than 0.1% causes, even by an optimal production method, shortage in the absolute amount of a fine Ni compound of 0.1 μm or less or ofNi contained as a solid solution or in the amount of the specific Sn-based compound. Accordingly, a content of 0.1% or more is necessary for effectively bringing out those effects of Ni.

[0082] However, ifNi is excessively contained to exceed 3.0%, a compound such as oxide, crystallized product or precipitate ofNi is coarsened or a coarse Ni compound increases, as a result, the amount of a fine Ni compound or the amount ofNi contained as a solid solution decreases. Also, the coarsened Ni compound becomes a starting point of fracture and leads to reduction not only in the strength or stress relaxation resistance characteristic but also in the elongation. Accordingly, the Ni content is specified to be 0.1 to 3.0%, preferably 0.3 to 2.0%.

(Sn)

[0083] Sn is contained as a solid solution in the copper alloy and thereby enhances the strength. Also, Sn forms the specific Sn-based compound related to the specific intensity peak in the X-ray diffraction pattern, specified in the first embodiment of the present invention. Furthermore, Sn contained as a solid solution in the matrix suppresses the softening due to recrystallization during annealing. If the Sn content is less than 0.01%, the strength-ductility balance cannot be enhanced due to a too small amount of Sn, whereas if the Sn content exceeds 3.0%, not only the electrical conductivity is significantly decreased but also Sn contained as a solid solution is segregated in the grain boundary to reduce the elongation. Accordingly, the Sn content is specified to be 0.01 to 3.0%, preferably 0.1 to 2.0%.

(P)

[0084] P is an element necessary for enhancing the strength or stress relaxation resistance characteristic by forming a fine precipitate with Ni. Also, P acts as a deoxidizing agent. A content of less than 0.01% causes shortage in the P-based fine precipitate particle and therefore, a content of 0.01% or more is necessary. However, if this element is excessively contained to exceed 0.3%, an Ni-P intermetallic compound precipitated particle is coarsened, which leads to reduction not only in the strength or stress relaxation resistance characteristic but also in the hot workability. Accordingly, the P content is specified to be 0.01 to 0.3%, preferably 0.02 to 0.2%.

(Fe, Zn, Mn, Si and Mg)

[0085] Fe, Zn, Mn, Si and Mg are impurities that readily intermix from a molten raw material such as scrap. These elements each produces an effect when contained but generally decreases the electrical conductivity. Also, if the content is increased, ingot making in a shaft furnace becomes difficult. Accordingly, in the case of obtaining a high electrical conductivity, the contents are specified to be 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. In other words, the contents lower than these upper limits are allowable in the first embodiment of the present invention.

[0086] Fe elevates the recrystallization temperature of the copper alloy, similarly to Sn. However, if its content exceeds 0.5%, the electrical conductivity decreases. The content is preferably 0.3% or less.

[0087] Zn prevents separation of tin plating. However, if its content exceeds 1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, in the case of ingot making in a shaft furnace, the content is preferably 0.05% or less. In the temperature region (from about 150 to 180°C) where the alloy sheet is used as an automotive terminal, the effect of preventing separation of tin plating can be obtained even with a content of 0.05% or less.

[0088] Mn and Si have an effect as a deoxidizing agent. However, if the content thereof exceeds 0.1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the contents are preferably 0.001% or less of Mn and 0.002% or less of Si.

[0089] Mg has an activity of enhancing the stress relaxation resistance characteristic. However, if its content exceeds 0.3%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the content is preferably 0.001% or less.

(Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt)

[0090] The copper alloy according to the first embodiment of the present invention is allowed to further contain at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in an amount of 1.0% or less in terms of a total amount of these elements. These elements have an activity of preventing coarsening of the grain but, if the amount of these elements exceeds 1.0% in total, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, ingot making in a shaft furnace becomes difficult.

[0091] In addition, Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal are also impurities, and the amount of these elements is preferably limited to 0.1% or less in total.

(Production Method of Copper Alloy Sheet)

[0092] The production method of the copper alloy sheet according to the first embodiment of the present invention is described below. In producing the copper alloy sheet according to the first embodiment of the present invention, the production method itself may be an ordinary method except for the conditions in the finish annealing step. That is, a molten copper alloy after adjusting the component composition is subjected to casting, ingot scalping, soaking and hot rolling and then repeatedly to cold rolling and annealing, whereby a final (product) sheet is obtained. However, preferred production conditions for producing the copper alloy sheet according to the first embodiment of the present invention are present, and these are described below.

[0093] In casting the above-described copper alloy composition according to the first embodiment of the present invention, high-productivity ingot making in a shaft furnace which is a large-scale melting furnace is possible. However, the time required is preferably as short as possible, such that the time required from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace is within 1,200 seconds and further, the time required from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling is within 1,200 seconds.

[0094] By virtue of shortening the time from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace and shortening the time from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling, generation of a coarse Ni compound can be suppressed and at the same time, the amount of a fine Ni compound or the amount ofNi contained as a solid solution can be ensured. In turn, as a premise, the copper alloy sheet can be assured of the electrical conductivity, stress relaxation resistance characteristic and strength.

[0095] Incidentally, even when it is intended to control the amount of a fine Ni compound or the amount ofNi contained as a solid solution mainly by the cold rolling conditions or annealing conditions in the later stage, the absolute amount of a fine Ni compound or of Ni contained as a solid solution already becomes small in the previous steps until the completion of hot rolling. Furthermore, in the case where the amount of a coarse Ni compound produced in the previous steps above is large, a fine product precipitated in the cold rolling and annealing steps is trapped by the coarse product and the amount of a fine product independently present in the matrix is more and more reduced. Accordingly, despite the large amount ofNi added, sufficiently high strength and excellent stress relaxation resistance characteristic may not be obtained.

[0096] Hot rolling may be performed in an ordinary manner. The inlet-side temperature of hot rolling is approximately from 600 to 1,000°C, and the finishing temperature is approximately from 600 to 850°C. After the hot rolling, water cooling or standing to cool is performed.

[0097] Thereafter, cold rolling and annealing are repeatedly performed to obtain a copper alloy sheet having a product sheet thickness. The annealing and cold rolling may be repeated according to the final (product) sheet thickness. In the cold rough rolling, the working ratio is selected so that a working ratio of approximately from 30 to 80% can be obtained in the final finish rolling. In the middle of the cold rough rolling, intermediate recrystallization annealing may be appropriately interposed.

(Finish Annealing)

[0098] In the copper alloy sheet according to the first embodiment of the present invention, as described above, the specific Sn-based compound of which intensity peak position in the X-ray diffraction pattern appears between 100° and 102° is produced by the characteristic control of the finish annealing conditions. As a result, a copper alloy sheet with excellent strength-ductility balance, where the electrical conductivity is enhanced more than the usually expected effect of elevating the electrical conductivity and the elongation of the obtained copper alloy sheet is enhanced while maintaining the stress relaxation resistance characteristic, is obtained without reducing the strength which usually decreases by the finish annealing. From a commonsense standpoint, the strength after finish annealing usually decreases due to a recovery/recrystallization phenomenon during finish annealing. However, under the characteristic control of finish annealing conditions, the strength is not reduced but is maintained and the elongation is rather enhanced. The electrical conductivity is also elevated.

[0099] As for the finish annealing temperature, the finish annealing is performed at a maximum peak temperature of 500 to 800°C in terms of the substantial temperature of the sheet, and the holding time in this temperature range is preferably from 10 to 60 seconds. The average temperature rise rate of the sheet to the maximum peak temperature is 50°C/s or more. Additionally, when cooling the sheet to room temperature, the average cooling rate of the sheet from 400°C to room temperature is from 40 to 100°C/h.

[0100] If the average temperature rise rate is too low and is less than 50°C/s, an Ni compound (precipitate) such as Ni-P is coarsened during the sheet temperature rise and the sheet cannot satisfy particularly the elongation, strength and stress relaxation resistance characteristic at the same time. The average temperature rise rate is preferably higher, and the upper limit thereof is determined by the equipment capacity of the annealing furnace used for the finish annealing.

[0101] Also, if the average cooling rate from 400°C to room temperature is too low and is less than 40°C/h, an Ni compound (precipitate) such as Ni-P is coarsened and the sheet cannot satisfy particularly the elongation, strength and stress relaxation resistance characteristic at the same time. Furthermore, if the average cooling rate is too low, as a serious issue, Ni as a solid solution is consumed preferentially for the growth of a coarsened Ni compound such as Ni-P. Then, the specific Sn-based compound is not produced and the intensity peak is not allowed to be present at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern of the copper alloy sheet. The grain is also coarsened and this causes reduction in the strength and elongation.

[0102] On the other hand, if the average cooling rate from 400°C to room temperature is too high and exceeds 100°C/h, a fine precipitate may be produced but, as a serious issue, similarly to the case of the average cooling rate being too low, the specific Sn-based compound is not produced and the specific intensity peak in the X-ray diffraction pattern of the copper alloy sheet is not present. In this way, if the average cooling rate from 400°C to room temperature is too low or too high, the elongation and strength in particular are decreased and a copper alloy sheet excellent in the electrical conductivity and strength-ductility balance cannot be obtained, failing in satisfying these properties including the stress relaxation resistance characteristic all at the same time.

[0103] At the cooling from the maximum peak temperature, the average cooling rate of the sheet on the high temperature side down to 400°C can be freely selected. However, in view of preventing both reduction in the efficiency of the annealing step and coarsening of the grain size, the average cooling rate is preferably 100°C/h or more.

[0104] The strain relief annealing or stabilizing annealing after the final finish cold rolling is preferably performed under the conditions of a substantial temperature of 250 to 450°C x from 20 to 40 seconds. By this annealing, the strain introduced in the final finish rolling can be removed. At the same time, softening of the material does not occur and reduction in the strength can be suppressed.

(2) Best Mode for Carrying Out Second Embodiment of the Present Invention

[0105] In the next place, the second embodiment of the present invention is described in detail below.

(X-Ray Diffraction Intensity Ratio)

[0106] The X-ray diffraction intensity ratio in the second embodiment of the present invention is determined as follows. The X-ray diffraction intensity I(200) from (200) plane as the Cube orientation in the sheet surface and the X-ray diffraction intensity I(220) from (220) plane as the orientation except for the Cube orientation are measured using a normal X-ray diffraction method, and the ratio of these X-ray diffraction intensities (X-ray diffraction peak ratio), I(200)/I(220) can be determined from these.

[0107] The texture of a normal copper alloy sheet is composed of a fairly large number of orientation factors and when the constituent ratio of these factors is varied, the plastic anisotropy of the sheet material and the stress relaxation resistance characteristic are changed. Out of these factors, the orientation density of Cube orientation [hereinafter sometimes referred to as D(Cube)] and a specific crystal orientation density other than that are controlled to appropriate ranges, whereby the anisotropy in a specific direction such as parallel direction or orthogonal direction with respect to the rolling direction is reduced.

[0108] That is, the development of Cube orientation is suppressed and the development of a specific crystal orientation other than Cube orientation is intensified. By this control, the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction is enhanced, and the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction is made small. Furthermore, even if the blanking is performed in either one direction of parallel direction and orthogonal direction with respect to the rolling direction, the stress relaxation resistance characteristic is high in the direction orthogonal to the rolling direction as well as in the direction parallel to the rolling direction, so that the stress relaxation resistance characteristic as a terminal or connector can be satisfied irrespective of the blanking direction of the raw material copper alloy sheet.

[0109] Accordingly, in the second embodiment of the present invention, the ratio I(200)/I(220) of the X-ray diffraction intensity I(200) from (200) plane as Cube orientation in the sheet surface to the X-ray diffraction intensity I(220) from (220) plane as an orientation other than Cube orientation is specified as 0.25 or less, preferably 0.20 or less.

[0110] If the ratio I(200)/I(220) exceeds 0.25, the Cube orientation is developed and the development of a specific crystal orientation other than Cube orientation is suppressed. Also, anisotropy in a specific direction such as parallel direction with respect to the rolling direction is intensified and the stress relaxation resistance characteristic in the orthogonal direction is rather not enhanced. Furthermore, the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction cannot be made small and anisotropy (difference in the stress relaxation resistance characteristic) between these two directions becomes large.

(Average grain size)

[0111] In the second embodiment of the present invention, the control of the texture of the Cu-Ni-Sn-P-based copper alloy sheet is combined with the control for decreasing the average grain size to reduce the anisotropy in a specific direction such as parallel direction or orthogonal direction with respect to the rolling direction, whereby the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction is enhanced and at the same time, the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction is made small.

[0112] Accordingly, in the second embodiment of the present invention, the average grain size is made fine as 5.0 μm or less. If the average grain size is coarsened to exceed 5.0 μm, despite the above-described control of the texture, anisotropy in a specific direction such as parallel direction with respect to the rolling direction is intensified and the stress relaxation resistance characteristic in the orthogonal direction is rather not enhanced. Furthermore, the difference in the stress relaxation resistance characteristic between the parallel direction and the orthogonal direction with respect to the rolling direction cannot be made small and anisotropy (difference in the stress relaxation resistance characteristic) between these two directions becomes large.

[0113] The average grain size can be measured in the process of measuring the distribution density of a specific orientation by a crystal orientation analysis method using FESEM/EBSP. That is, in this crystal orientation analysis method, the crystal orientation is analyzed based on the electron backscatter diffraction pattern (Kikuchi pattern) generated when an electron beam is obliquely applied to the sample surface. This method is also known as a high-resolution crystal orientation analysis (FESEM/EBSP) method for the analysis of crystal orientation of a diamond thin film, a copper alloy or the like. A case of performing the crystal orientation analysis of a copper alloy by this method similarly to the second embodiment of the present invention is disclosed, for example, in JP-A-2005-29857 and 2005-139501.

[0114] As for the procedure of analysis by this crystal orientation analysis method, first, a measurement region of a material to be measured is usually partitioned into hexagonal regions or the like, and the partitioned regions each is determined for a Kikuchi pattern (specific orientation mapping) from the reflected electron of an electron beam injected into the sample surface. At this time, an electron beam is two-dimensionally scanned on the sample surface and the crystal orientation is measured at predetermined pitch intervals, whereby the orientation distribution in the sample surface can be measured.

[0115] Next, the obtained Kikuchi pattern is analyzed to determine the crystal orientation at the electron beam incident position. That is, the obtained Kikuchi pattern is compared with a known crystal structure data, and the crystal orientation at the measurement point is determined. The crystal orientation at a measurement point adjacent to the measurement point above is determined in the same manner, and those where the orientation difference between crystals adjacent to each other is within ± 10° (slippage within ± 10° from the crystal plane) are taken (regarded) as belonging to the same crystal plane. In the case where the orientation difference of two crystals exceeds ± 10°, the space therebetween (for example, the side at which two hexagons are contacted) is taken as a grain boundary. In this way, the distribution of grain boundaries in the sample surface is determined.

[0116] More specifically, a test specimen for the observation of texture is sampled from the produced copper alloy sheet and after mechanical polishing and buff polishing, the surface is regulated by electrolytic polishing. With respect to the thus-obtained test specimen, the average grain size of grains can be measured by using, for example, FESEM manufactured by JEOL Ltd. and the EBSP measurement/analysis system OIM (Orientation Imaging Macrograph) manufactured by TSL and using an analysis software (software name: "OIM Analysis") for the system. The range of measured view is set to, for example, a region of about 500 μm × 500 μm and after measuring the test specimen at an appropriate number of portions, the values are averaged.

(Copper Alloy Component Composition)

[0117] The component composition of the copper alloy according to the second embodiment of the present invention is described below. In the second embodiment of the present invention, as a premise, the component composition of the copper alloy is, as described above, a Cu-Ni-Sn-P-based alloy allowing for ingot making in a shaft furnace and because of its high productivity, enabling a great cost down.

[0118] In order to obtain a copper alloy that is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies the properties required for a connection component such as automotive terminal or connector and also that is excellent in the strength, stress relaxation resistance characteristic and electrical conductivity, the copper alloy fundamentally comprises 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% of P, with the balance being copper and inevitable impurities. The % indicative of the content of each element means mass%. The alloy elements of the copper alloy are described below by referring to the reasons of addition or restraint.

(Ni)

[0119] Ni is an element necessary for enhancing the strength or stress relaxation resistance characteristic by being present as a solid solution in the copper alloy matrix or forming a fine precipitate or compound with other alloy elements such as P. An Ni content of less than 0.1% causes, even by an optimal production method, shortage in the absolute amount of a fine Ni compound of 0.1 μm or less or ofNi contained as a solid solution. Accordingly, a content of 0.1% or more is necessary for effectively bringing out those effects ofNi.

[0120] However, ifNi is excessively contained to exceed 3.0%, a compound such as oxide, crystallized product or precipitate ofNi is coarsened or a coarse Ni compound increases, as a result, the amount of a fine Ni compound or the amount ofNi contained as a solid solution rather decreases. The coarsened Ni compound becomes a starting point of fracture and leads to reduction in the strength or bendability. Accordingly, the Ni content is specified to be 0.1 to 3.0%, preferably 0.3 to 2.0%.

(Sn)

[0121] Sn is contained as a solid solution in the copper alloy matrix and thereby enhances the strength. Also, Sn contained as a solid solution suppresses the softening due to recrystallization during annealing. If the Sn content is less than 0.01%, the amount of Sn is too small and the strength cannot be enhanced, whereas if the Sn content exceeds 3.0%, not only the electrical conductivity is significantly decreased but also Sn contained as a solid solution is segregated in the grain boundary to reduce the strength or bendability. Accordingly, the Sn content is specified to be 0.01 to 3.0%, preferably 0.1 to 2.0%.

(P)

[0122] P is an element necessary for enhancing the strength or stress relaxation resistance characteristic by forming a fine precipitate with Ni. Also, P acts as a deoxidizing agent. A content of less than 0.01% causes shortage in the P-based fine precipitate particle and therefore, a content of 0.01% or more is necessary. However, if this element is excessively contained to exceed 0.3%, an Ni-P intermetallic compound precipitated particle is coarsened, which leads to reduction not only in the strength or stress relaxation resistance characteristic but also in the hot workability. Accordingly, the P content is specified to be 0.01 to 0.3%, preferably 0.02 to 0.2%.

(Fe, Zn, Mn, Si and Mg)

[0123] Fe, Zn, Mn, Si and Mg are impurities that readily intermix from a molten raw material such as scrap. These elements each produces an effect when contained but generally decreases the electrical conductivity. Also, if the content is increased, ingot making in a shaft furnace becomes difficult. Accordingly, in the case of obtaining a high electrical conductivity, the contents are specified to be 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. In other words, the contents lower than these upper limits are allowable in the second embodiment of the present invention.

[0124] Fe elevates the recrystallization temperature of the copper alloy, similarly to Sn. However, if its content exceeds 0.5%, the electrical conductivity decreases. The content is preferably 0.3% or less.

[0125] Zn prevents separation of tin plating. However, if its content exceeds 1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, in the case of ingot making in a shaft furnace, the content is preferably 0.05% or less. In the temperature region (from about 150 to 180°C) where the alloy sheet is used as an automotive terminal, the effect of preventing separation of tin plating can be obtained even with a content of 0.05% or less.

[0126] Mn and Si have an effect as a deoxidizing agent. However, if the content thereof exceeds 0.1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the contents are preferably 0.001% or less of Mn and 0.002% or less of Si.

[0127] Mg has an activity of enhancing the stress relaxation resistance characteristic. However, if its content exceeds 0.3%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the content is preferably 0.001% or less.

(Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt)

[0128] The copper alloy according to the second embodiment of the present invention is allowed to further contain at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in an amount of 1.0% or less in terms of a total amount of these elements. These elements have an activity of preventing coarsening of the grain but, if the amount of these elements exceeds 1.0% in total, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, ingot making in a shaft furnace becomes difficult.

[0129] In addition, Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal are also impurities, and the amount of these elements is preferably limited to 0.1% or less in total.

(Production Method of Copper Alloy Sheet)

[0130] The production method of the copper alloy sheet according to the second embodiment of the present invention is described below. In producing the copper alloy sheet according to the second embodiment of the present invention, the production method itself may be an ordinary method except for the conditions in the finish annealing step. That is, a molten copper alloy after adjusting the component composition is subjected to casting, ingot scalping, soaking and hot rolling and then repeatedly to cold rolling and annealing, whereby a final (product) sheet is obtained. However, preferred production conditions are present for allowing the copper alloy sheet according to the second embodiment of the present invention to obtain necessary properties such as strength and stress relaxation resistance characteristic, and these are described below. Also, in order to compose the texture of the copper alloy sheet according to the second embodiment of the present invention, as described later, it is necessary to perform final cold rolling and subsequent final low-temperature annealing in combination and control the conditions in each of these steps.

[0131] In casting the above-described copper alloy composition according to the second embodiment of the present invention, high-productivity ingot making in a shaft furnace which is a large-scale melting furnace is possible. However, the time required is preferably as short as possible, such that the time required from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace is within 1,200 seconds and further, the time required from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling is within 1,200 seconds.

[0132] By virtue of shortening the time from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace and shortening the time from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling, generation of a coarse Ni compound can be suppressed and at the same time, the amount of a fine Ni compound or the amount ofNi contained as a solid solution can be ensured. As a result, the copper alloy sheet can be assured of the electrical conductivity, stress relaxation resistance characteristic and strength.

[0133] Incidentally, even when it is intended to control the amount of a fine Ni compound or the amount ofNi contained as a solid solution mainly by the cold rolling conditions or annealing conditions in the later stage, the absolute amount of a fine Ni compound or of Ni contained as a solid solution already becomes small in the previous steps until the completion of hot rolling. Furthermore, in the case where the amount of a coarse Ni compound produced in the previous steps above is large, a fine product precipitated in the cold rolling and annealing steps is trapped by the coarse product and the amount of a fine product independently present in the matrix is more and more reduced. Accordingly, despite the large amount ofNi added, sufficiently high strength and excellent stress relaxation resistance characteristic may not be obtained.

[0134] Hot rolling may be performed in an ordinary manner. The inlet-side temperature of hot rolling is approximately from 600 to 1,000°C, and the finishing temperature is approximately from 600 to 850°C. After the hot rolling, water cooling or standing to cool is performed.

[0135] Thereafter, cold rolling and annealing are repeatedly performed to obtain a copper alloy sheet having a product sheet thickness. The annealing and cold rolling may be repeated according to the final (product) sheet thickness. In the cold rolling, the working ratio is selected so that a working ratio of approximately from 30 to 80% can be obtained in the final finish rolling. In the middle of the cold rolling, intermediate recrystallization annealing may be appropriately interposed.

[0136] As for the finish annealing temperature, the finish annealing is preferably performed at a maximum peak temperature of 500 to 800°C in terms of the substantial temperature of the sheet, and the holding time in this temperature range is preferably from 10 to 60 seconds.

(Final Cold Rolling)

[0137] In the final cold rolling, the rolling speed is set large and is 200 m/min or more. In combination with this, as described later, final annealing at a low temperature is performed. By increasing the rolling speed in the final cold rolling, the strain rate introduced into the Cu-Ni-Sn-P-based copper alloy is increased and this allows a crystal orientation other than Cube orientation to readily develop and suppresses the development of Cube orientation, so that anisotropy of the stress relaxation resistance characteristic can be reduced. Also, randomization of the crystal orientation is accelerated and since a group of the same orientation grains (grains close in the crystal orientation come adjacent to each other and form a group) is reduced, the grain size of individual grain also becomes fine. Accordingly, the X-ray diffraction intensity ratio I(200)/I(220) in the surface of the Cu-Ni-Sn-P-based copper alloy sheet can be made to be 0.25 or less, and a fine average grain size of 5.0 μm or less can be obtained. As a result, the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction can be enhanced and the difference from the stress relaxation ratio in the direction parallel to the rolling direction can also be made small.

[0138] If the rolling speed in the final cold rolling is too small and is less than 200 m/min, the strain rate is small and in the Cu-Ni-Sn-P-based copper alloy sheet like the second embodiment of the present invention, the development of a crystal orientation other than Cube orientation is suppressed or a group of the same orientation grains is readily formed, giving rise to an increase in the grain size of individual grains. Therefore, the X-ray diffraction intensity ratio I(200)/I(220) cannot be made to be 0.25 or less and the average grain size is also readily coarsened to exceed 5.0 μm.

[0139] As for the number of passes in the final cold rolling, the rolling is preferably performed usually in 3 or 4 passes while avoiding an excessively small or large number of passes. Also, the rolling reduction per pass need not exceed 50% and each rolling reduction per pass is determined by taking into consideration the original sheet thickness, final sheet thickness after cold rolling, number of passes, and maximum rolling reduction.

(Final Annealing)

[0140] In the production of the copper alloy according to the second embodiment of the present invention, final annealing at a low temperature is performed in a continuous heat-treating furnace after the final cold rolling. In the continuous annealing step using a continuous heat-treating furnace, low-temperature annealing can be performed in a short time at a maximum peak temperature of 100 to 400°C by controlling the sheet passage rate of the sheet passing through the furnace. In this respect, when the sheet passage rate is set to be from 10 to 100 m/min at the above-described maximum peak temperature of 100 to 400°C, the development of Cube orientation of the Cu-Ni-Sn-P-based copper alloy sheet is suppressed, whereas the development of a specific crystal orientation other than Cube orientation is intensified, so that anisotropy can be reduced. Also, the growth of a grain can be suppressed. Accordingly, the X-ray diffraction intensity I (200)/I(220) in the surface of the Cu-Ni-Sn-P-based copper alloy sheet can be made to be 0.25 or less and a fine average grain size of 5.0 μm or less can be obtained. As a result, the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction can be enhanced and the difference from the stress relaxation ratio in the direction parallel to the rolling direction can also be made small.

[0141] If the sheet passage rate exceeds 100 m/min, an abrupt temperature change of the sheet occurs from room temperature to the maximum peak temperature of 100 to 400°C and therefore, the residual strain amount remaining in the sheet after passing the furnace is increased, allowing easy occurrence of a rearrangement or recovery phenomenon of dislocations. That is, the stress relaxation resistance characteristic decreases in both the orthogonal direction and the parallel direction with respect to the rolling direction. On the other hand, if the sheet passage rate is less than 10 m/min, not only the processing time in the above-described maximum peak temperature range of 100 to 400°C is too long but also because of a small temperature rise or drop rate, in the Cu-Ni-Sn-P-based copper alloy sheet like the second embodiment of the present invention, the development of a crystal orientation other than Cube orientation is particularly suppressed and the growth of a grain is accelerated. Consequently, anisotropy of the stress relaxation resistance characteristic is intensified and the X-ray diffraction intensity ratio I(200)/I(220) cannot be made to be 0.25 or less, as a result, the average grain size is readily coarsened to exceed 5.0 μm.

[0142] Also, if the annealing temperature is less than 100°C or the above-described low-temperature annealing is not performed, there is a high possibility that the texture/properties of the copper alloy sheet are scarcely changed from the state after the final cold rolling. On the contrary, if the annealing temperature exceeds 400°C, this incurs recrystallization, excessive occurrence of a rearrangement or recovery phenomenon of dislocations or coarsening of the precipitate and therefore, the strength is highly likely to decrease.

(3) Best Mode for Carrying Out Third Embodiment of the Present Invention

[0143] In the next place, the third embodiment of the present invention is described in detail below.

(Measurement of Orientation Distribution Density)

[0144] In the third embodiment of the present invention, the distribution density of B orientation and the sum of distribution densities of B orientation, S orientation and Cu orientation are measured by a crystal orientation analysis method using an electron backscatter diffraction pattern EBSP through a field emission scanning electron microscope FESEM.

[0145] In specifying the orientation density of each of these orientations, the orientation density is measured by a crystal orientation analysis method using EBSP, because for enhancing the stress relaxation resistance characteristic or bendability while maintaining high strength, this is affected by the texture (aggregate texture) in a more microscopic region of the sheet (sheet surface). In the crystal orientation analysis method using EBSP, the texture in a microscopic region can be quantified.

[0146] On the other hand, in the X-ray diffraction (e.g., X-ray diffraction intensity) generally employed for specifying or measuring the texture, a texture (aggregate texture) in a relatively macroscopic region is measured as compared with the crystal orientation analysis method using EBSP. Accordingly, the texture (aggregate texture) in a microscopic region cannot be measured accurately.

[0147] In the crystal orientation analysis method using an electron backscatter diffraction pattern EBSP, the crystal orientation is analyzed based on the electron backscatter diffraction pattern (Kikuchi pattern) generated when an electron beam is obliquely applied to the sample surface. This method is also known as a high-resolution crystal orientation analysis (FESEM/EBSP) method for the analysis of crystal orientation of a diamond thin film, a copper alloy or the like. A case of performing the crystal orientation analysis of a copper alloy by this method similarly to the third embodiment of the present invention is disclosed, for example, in JP-A-2005-29857 and 2005-139501.

[0148] As for the procedure of analysis by this crystal orientation analysis method, first, a measurement region of a material to be measured is usually partitioned into hexagonal regions or the like, and the partitioned regions each is determined for a Kikuchi pattern from the reflected electron of an electron beam injected into the sample surface. At this time, an electron beam is two-dimensionally scanned on the sample surface and the crystal orientation is measured at predetermined pitch intervals, whereby the orientation distribution in the sample surface can be measured.

[0149] Next, the obtained Kikuchi pattern is analyzed to determine the crystal orientation at the electron beam incident position. That is, the obtained Kikuchi pattern is compared with a known crystal structure data, and the crystal orientation at the measurement point is determined. The crystal orientation at a measurement point adjacent to the measurement point above is determined in the same manner, and those where the orientation difference between crystals adjacent to each other is within ±15° (slippage within ±10° from the crystal plane) are taken (regarded) as belonging to the same crystal plane.

[0150] More specifically, a test specimen for the observation of texture is sampled from the produced copper alloy sheet and after mechanical polishing and buff polishing, the surface is regulated by electrolytic polishing. With respect to the thus-obtained test specimen, whether or not the orientation of each grain is the objective orientation (within 10° from the ideal orientation) is judged using, for example, FESEM manufactured by JEOL Ltd. and the EBSP measurement/analysis system OIM (Orientation Imaging Macrograph) manufactured by TSL and using an analysis software (software name: "OIM Analysis") for the system, and the orientation density in the measured view is determined.

[0151] The range of measured view is a fine (microscopic) region of about 500 μm × 500 μm and is an extremely fine region as compared with the measuring range of X-ray diffraction. Accordingly, the orientation density of the texture in a more microscopic region of the sheet, which affects the stress relaxation resistance characteristic or bendability, can be measured in greater detail with higher precision as described above than in the measurement of orientation density by the X-ray diffraction.

[0152] Incidentally, since the orientation distribution is changed in the sheet thickness direction, it is preferred to measure the orientation distribution density at arbitrary several points in the sheet thickness direction and average the values obtained. However, the connection component such as automotive terminal or connector is a thin sheet having a thickness of about 0.1 to 0.3 mm and therefore, the value measured with the sheet thickness may be directly evaluated.

(Significance of Orientation Distribution Density)

[0153] In the third embodiment of the present invention, for enhancing the stress relaxation resistance characteristic or bendability while maintaining high strength in a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, as described above, the distribution density of B orientation is reduced and at the same time, the sum of distribution densities ofB orientation, S orientation and Cu orientation is controlled to a specific range.

[0154] Accordingly, in the third embodiment of the present invention, the texture of the copper alloy sheet is specified such that the distribution density of B orientation is 40% or less and the sum of distribution densities ofB orientation, S orientation and Cu orientation is 30 to 90%.

[0155] If the distribution density ofB orientation exceeds 30% or the sum of distribution densities of B orientation, S orientation and Cu orientation exceeds 90%, as described in Examples later, the bendability cannot be enhanced with the above-described high strength.

[0156] On the other hand, in order to set the sum of distribution densities of B orientation, S orientation and Cu orientation to be less than 30%, this requires reducing the work-hardened amount in the cold rolling. Accordingly, if the sum of distribution densities ofB orientation, S orientation and Cu orientation is less than 30%, as described in Examples later, the bendability may be enhanced but high strength cannot be achieved and the strength required in usage as a terminal or connector becomes insufficient.

[0157] As regards the Cu-Ni-Sn-P-based copper alloy sheet, in a normal sheet made to have high strength by increasing the work-hardened amount in the heavy working of cold rolling, excessive development of the rolled texture inevitably results and therefore, the distribution density ofB orientation is necessarily liable to become large and exceed 40%. Incidentally, this development of the rolled texture also affects other orientation densities such as Cube orientation. However, particularly, in the region of a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, the effect of development of Cu orientation, B orientation and S orientation on the bendability is by far higher than the effect of other orientations such as Cube orientation.

(Copper Alloy Component Composition)

[0158] The component composition of the copper alloy according to the third embodiment of the present invention is described below. In the third embodiment of the present invention, as a premise, the component composition of the copper alloy is, as described above, a Cu-Ni-Sn-P-based alloy allowing for ingot making in a shaft furnace and because of its high productivity, enabling a great cost down.

[0159] In order to obtain a copper alloy that is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies the properties required for a connection component such as automotive terminal or connector and also that is excellent in the strength, stress relaxation resistance characteristic, electrical conductivity and bendability, the copper alloy fundamentally comprises 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn, and 0.01 to 0.3% of P, with the balance being copper and inevitable impurities. The % indicative of the content of each element means mass%. The alloy elements of the copper alloy are described below by referring to the reasons of addition or restraint.

(Ni)

[0160] Ni is an element necessary for enhancing the strength or stress relaxation resistance characteristic by being present as a solid solution in the copper alloy matrix or forming a fine precipitate or compound with other alloy elements such as P. An Ni content of less than 0.1% causes, even by an optimal production method, shortage in the absolute amount of a fine Ni compound of 0.1 μm or less or ofNi contained as a solid solution. Accordingly, a content of 0.1% or more is necessary for effectively bringing out those effects ofNi.

[0161] However, ifNi is excessively contained to exceed 3.0%, a compound such as oxide, crystallized product or precipitate ofNi is coarsened or a coarse Ni compound increases, as a result, the amount of a fine Ni compound or the amount ofNi contained as a solid solution rather decreases. The coarsened Ni compound becomes a starting point of fracture and leads to reduction in the strength or bendability. Accordingly, the Ni content is specified to be 0.1 to 3.0%, preferably 0.3 to 2.0%.

(Sn)

[0162] Sn is contained as a solid solution in the copper alloy matrix and thereby enhances the strength. Also, Sn contained as a solid solution suppresses the softening due to recrystallization during annealing. If the Sn content is less than 0.01%, the amount of Sn is too small and the strength cannot be enhanced, whereas if the Sn content exceeds 3.0%, not only the electrical conductivity is significantly decreased but also Sn contained as a solid solution is segregated in the grain boundary to reduce the strength or bendability. Accordingly, the Sn content is specified to be 0.01 to 3.0%, preferably 0.1 to 2.0%.

(P)

[0163] P is an element necessary for enhancing the strength or stress relaxation resistance characteristic by forming a fine precipitate with Ni. Also, P acts as a deoxidizing agent. A content of less than 0.01% causes shortage in the P-based fine precipitate particle and therefore, a content of 0.01% or more is necessary. However, if this element is excessively contained to exceed 0.3%, an Ni-P intermetallic compound precipitated particle is coarsened, which leads to reduction not only in the strength or stress relaxation resistance characteristic but also in the hot workability. Accordingly, the P content is specified to be 0.01 to 0.3%, preferably 0.02 to 0.2%.

(Fe, Zn, Mn, Si and Mg)

[0164] Fe, Zn, Mn, Si and Mg are impurities that readily intermix from a molten raw material such as scrap. These elements each produces an effect when contained but generally decreases the electrical conductivity. Also, if the content is increased, ingot making in a shaft furnace becomes difficult. Accordingly, in the case of obtaining a high electrical conductivity, the contents are specified to be 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. In other words, the contents lower than these upper limits are allowable in the third embodiment of the present invention.

[0165] Fe elevates the recrystallization temperature of the copper alloy, similarly to Sn. However, if its content exceeds 0.5%, the electrical conductivity decreases. The content is preferably 0.3% or less.

[0166] Zn prevents separation of tin plating. However, if its content exceeds 1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, in the case of ingot making in a shaft furnace, the content is preferably 0.05% or less. In the temperature region (from about 150 to 180°C) where the alloy sheet is used as an automotive terminal, the effect of preventing separation of tin plating can be obtained even with a content of 0.05% or less.

[0167] Mn and Si have an effect as a deoxidizing agent. However, if the content thereof exceeds 0.1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the contents are preferably 0.001% or less of Mn and 0.002% or less of Si.

[0168] Mg has an activity of enhancing the stress relaxation resistance characteristic. However, if its content exceeds 0.3%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the content is preferably 0.001% or less.

(Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt)

[0169] The copper alloy according to the third embodiment of the present invention is allowed to further contain at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in an amount of 1.0% or less as a total amount of these elements. These elements have an activity of preventing coarsening of the grain but, if the amount of these elements exceeds 1.0% in total, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, ingot making in a shaft furnace becomes difficult.

[0170] In addition, Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal are also impurities, and the amount of these elements is preferably limited to 0.1% or less in total.

(Production Method of Copper Alloy Sheet)

[0171] The production method of the copper alloy sheet according to the third embodiment of the present invention is described below. In producing the copper alloy sheet according to the third embodiment of the present invention, the production method itself may be an ordinary method except for the conditions in the finish annealing step. That is, a molten copper alloy after adjusting the component composition is subjected to casting, ingot scalping, soaking and hot rolling and then repeatedly to cold rolling and annealing, whereby a final (product) sheet is obtained. However, preferred production conditions are present for allowing the copper alloy sheet according to the third embodiment of the present invention to obtain necessary properties such as strength, stress relaxation resistance characteristic and bendability, and these are described below. Also, in order to compose the texture of the copper alloy sheet according to the third embodiment of the present invention, as described later, it is necessary to perform final cold rolling and subsequent final low-temperature annealing in combination and control the conditions in each of these steps.

[0172] In casting the above-described copper alloy composition according to the third embodiment of the present invention, high-productivity ingot making in a shaft furnace which is a large-scale melting furnace is possible. However, the time required is preferably as short as possible, such that the time required from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace is within 1,200 seconds and further, the time required from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling is within 1,200 seconds.

[0173] By virtue of shortening the time from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace and shortening the time from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling, generation of a coarse Ni compound can be suppressed and at the same time, the amount of a fine Ni compound or the amount ofNi contained as a solid solution can be ensured. As a result, the copper alloy sheet can be assured of the electrical conductivity, stress relaxation resistance characteristic and strength.

[0174] Incidentally, even when it is intended to control the amount of a fine Ni compound or the amount ofNi contained as a solid solution mainly by the cold rolling conditions or annealing conditions in the later stage, the absolute amount of a fine Ni compound or ofNi contained as a solid solution already becomes small in the previous steps until the completion of hot rolling. Furthermore, in the case where the amount of a coarse Ni compound produced in the previous steps above is large, a fine product precipitated in the cold rolling and annealing steps is trapped by the coarse product and the amount of a fine product independently present in the matrix is more and more reduced. Accordingly, despite the large amount ofNi added, sufficiently high strength and excellent stress relaxation resistance characteristic may not be obtained.

[0175] Hot rolling may be performed in an ordinary manner. The inlet-side temperature of hot rolling is approximately from 600 to 1,000°C, and the finishing temperature is approximately from 600 to 850°C. After the hot rolling, water cooling or standing to cool is performed.

[0176] Thereafter, cold rolling and annealing are repeatedly performed to obtain a copper alloy sheet having a product sheet thickness. The annealing and cold rolling may be repeated according to the final (product) sheet thickness. In the cold rolling, the working ratio is selected so that a working ratio of approximately from 30 to 80% can be obtained in the final finish rolling. In the middle of the cold rolling, intermediate recrystallization annealing may be appropriately interposed.

[0177] As for the finish annealing temperature, the finish annealing is preferably performed at a maximum peak temperature of 500 to 800°C in terms of the substantial temperature of the sheet, and the holding time in this temperature range is preferably from 10 to 60 seconds.

(Final Cold Rolling)

[0178] In order to obtain a high-strength Cu-Ni-Sn-P-based copper alloy sheet with a 0.2%-proof stress of 500 MPa or more, also in the third embodiment of the present invention, increase in the work-hardened amount (dense accumulation of introduced dislocations by the Orowan mechanism) by the heavy working of final cold rolling is effected. However, for allowing the texture of the copper alloy sheet to satisfy the conditions that the distribution density ofB orientation is 40% or less and the sum of distribution densities ofB orientation, S orientation and Cu orientation is from 30 to 90% and preventing the rolled texture from excessively developing outside of the ranges above, the cold rolling ratio (rolling reduction) per pass of the final cold rolling needs to be controlled.

[0179] Namely, the cold rolling ratio per pass of the final cold rolling is specified to be from 10 to 50%. As for the number of passes in the final cold rolling, the rolling is preferably performed usually in 3 or 4 passes while avoiding an excessively small or large number of passes.

[0180] With this normal number of passes, if the cold rolling ratio per pass of the final cold rolling exceeds 50%, there is a high possibility that the distribution density ofB orientation exceeds 40% or the sum of distribution densities of B orientation, S orientation and Cu orientation becomes large to exceed 90%, though this may vary depending on the component composition of the copper alloy or the past production history or production conditions.

[0181] On the other hand, if the cold rolling ratio per pass of the final cold rolling is less than 10%, the sum of distribution densities of B orientation, S orientation and Cu orientation is liable to be less than 30% and the work-hardened amount in the cold rolling has a high possibility of becoming insufficient. In turn, it is likely impossible to satisfy the above-described high strength or enhance the stress relaxation resistance characteristic or bendability.

(Final Annealing)

[0182] Based on the knowledge above, the final annealing is performed in a continuous heat-treating furnace, whereby the texture specified in the third embodiment of the present invention can be composed and the stress relaxation resistance characteristic and bendability can be enhanced while maintaining the high strength. That is, in the continuous heat-treating furnace, the tension imposed on the sheet when passing can be controlled and in turn, the texture of the copper alloy sheet can be controlled to a rolled texture where the distribution density of B orientation is 40% or less and the sum of distribution densities ofB orientation, S orientation and Cu orientation is from 30 to 90%. The tension imposed on the sheet when passing in the continuous heat-treating furnace greatly affects the distribution density of Brass orientation (B orientation).

[0183] In order to obtain the texture specified in the third embodiment of the present invention, the tension imposed on the copper alloy sheet when passing during final annealing in the continuous heat-treating furnace is controlled in the range of 0.1 to 8 kgf/mm^2. If the tension on passing of the sheet is out of this range, there is a high possibility that the texture specified in the third embodiment of the present invention is not composed.

[0184] The temperature of the final annealing in the continuous heat-treating furnace is preferably from 100 to 400°C. If the annealing temperature is a temperature condition of less than 100°C, this is the same as not performing the low-temperature annealing and the texture/properties of the copper alloy sheet have a high possibility of scarcely changing from the state after the final cold rolling. Conversely, if the annealing is performed at an annealing temperature exceeding 400°C, this incurs recrystallization, excessive occurrence of a rearrangement or recovery phenomenon of dislocations or coarsening of the precipitate and therefore, the texture specified in the third embodiment of the present invention may not be composed. Also, the strength is highly likely to decrease.

(4) Best Mode for Carrying Out Fourth Embodiment of the Present Invention

[0185] In the next place, the fourth embodiment of the present invention is described in detail below.

(Half-Value Breadth)

[0186] In the fourth embodiment of the present invention, for enhancing the press punchability, the copper alloy sheet is specified to have a dislocation density in not less than a given amount such that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the Cu-Ni-Sn-P-based copper alloy sheet surface by the peak height is 1.0×10^{-4} or more. By this construction, the stress relaxation resistance characteristic and press punchability of the Cu-Ni-Sn-P-based copper alloy sheet can be enhanced.

[0187] If the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak by the peak height is less than 1.0×10^{-4}, the dislocation density introduced into the sheet is reduced, making a little difference from the conventional Cu-Ni-Sn-P-based with a small dislocation density, and the stress relaxation resistance characteristic and press punchability are decreased or not enhanced.

[0188] As is well known, the half-value breadth is defined as a width (β) of the X-ray diffraction intensity peak at the position half (height: H/2) the X-ray diffraction intensity peak (height: H) shown in a schematic view of Fig. 5 where the ordinate indicates the X-ray diffraction intensity and the abscissa indicates the angle (2θ).

[0189] Incidentally, the half-value breadth of the X-ray diffraction intensity peak is usually used for determining or quantifying the crystallinity or non-crystallinity of metal surface, the crystallite size or the lattice strain. On the other hand, in the fourth embodiment of the present invention, as described above, the dislocation density that cannot be directly observed or quantified is specified using the value (β/H) obtained by dividing the half-value breadth β of the X-ray diffraction intensity peak from {200} plane in the sheet surface, which is fairly well correlated to the dislocation density, by the peak height H.

[0190] As for the X-ray diffraction intensity peak of the Cu-Ni-Sn-P-based copper alloy sheet surface, the half-value breadth (β) or peak height (H) of the X-ray diffraction intensity peak from other {220} plane is largest. However, when the height of the X-ray diffraction intensity peak is large (high), the peak height which divides the half-value breadth is also large and this is disadvantageous in that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak by the peak height becomes too small and many errors occur in the value itself, giving rise to poor reproducibility. For this reason, in the fourth embodiment of the present invention, the X-ray diffraction intensity peak from {200} plane, ensuring that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak by the peak height is large (the peak height is not large and the half-value breadth is fairly large), is employed.

[0191] Accordingly, in the fourth embodiment of the present invention, the issue is absolutely the introduced state of dislocation intensity into the sheet and it is not intended to control the accumulation ratio in texture, the grain size on sheet surface or the rolled texture by the above-described X-ray diffraction intensity peak from a specific crystal plane in the sheet surface. In other words, the introduced state of dislocation intensity into the sheet cannot be specified or controlled by this X-ray diffraction intensity peak from a specific crystal plane in the sheet surface or the control of the accumulation ratio in texture, the grain size on sheet surface or the rolled texture.

(Introduction of Dislocation Density)

[0192] In order to introduce a dislocation density such that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the Cu-Ni-Sn-P-based copper alloy sheet surface by the peak height is 1.0×10^{-4} or more, as described later, the strain amount introduced in the final cold rolling is increased. That is, in the final cold rolling, a technique such as use of a small-size roll having a roll diameter of less than 80 mmϕ or setting of the rolling reduction (cold rolling ratio) per pass to 20% or more is selected and used, or these techniques are used in combination.

(Burr Height)

[0193] In the fourth embodiment of the present invention, the press punchability is exactly evaluated by the "burr height" generated in a press punching test of punching a circular round hole in a copper alloy sheet according to Japan Copper and Brass Association Technical Standards JCBA T310 "Shear Test Method of Copper and Copper Alloy Thin Sheet Materials". When the burr height is 5 μm or less, the press punchability of the Cu-Ni-Sn-P-based copper alloy sheet can be rated as good.

[0194] At this time, in order to impart reproducibility to the measurement of a shear plane ratio in the press punching test, test conditions enabling assurance of the reproducibility in the above-described press punching test are specifically specified. That is, in the press punching test, a punching press shown in Fig. 6(a) is used, and a copper alloy sheet (test specimen, material to be worked) held on the top of a die having a circular round hole, which is supported by a die holder, is punched from the upper side to the down side by a 10 mmϕ punch. The clearance with the punch is set to 3%, and the copper alloy sheet is fixed to the die top from the upper part by a platelike stopper. A lubricating oil, UNIPRESS PA5, produced by Nisseki Mitsubishi is used. The construction material of the punch and die is SKS-3, the die cutter length is 5 mm, and the punching die taper is 0°.

[0195] Fig. 6(b) shows the side cross-section of the punched hole generated in the copper alloy sheet by the punching above. The side cross-section of the punched hole is observed through a scanning microscope, and the "burr height" (height of burr or flash: μm) projecting downward in the peripheral part at the bottom of the punched hole is measured. At this time, as for the "burr height" per one punched hole, values at 4 points created by 90° dividing the circumference of the circular punched hole are averaged and furthermore, by punching 6 sheets (6 pieces) for each copper alloy sheet, an average of these sheets is taken as the "burr height" (μm). In Fig. 6(b), t is the thickness of the copper alloy sheet, a is the shear plane of the punched hole, b is a fracture plane of punched hole, and c is a shear droop generated in the peripheral part at the top of the punched hole.

(Copper Alloy Component Composition)

[0196] The component composition of the copper alloy according to the fourth embodiment of the present invention is described below. In the fourth embodiment of the present invention, as a premise, the component composition of the copper alloy is, as described above, a Cu-Ni-Sn-P-based alloy allowing for ingot making in a shaft furnace and because of its high productivity, enabling a great cost down.

[0197] In order to obtain a copper alloy that is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies the properties required for a connection component such as automotive terminal or connector and also that is excellent in the strength, stress relaxation resistance characteristic and electrical conductivity, the copper alloy fundamentally comprises 0.1 to 3.0% ofNi, 0.01 to 3.0% of Sn and 0.01 to 0.3% of P, with the balance being copper and inevitable impurities.

[0198] The % indicative of the content of each element means mass% including the indication in the claims. The alloy elements of the copper alloy according to the fourth embodiment of the present invention are described below by referring to the reasons of incorporation (addition) or restraint.

(Ni)

[0199] Ni is an element necessary for enhancing the strength or stress relaxation resistance characteristic by being present as a solid solution in the copper alloy matrix or forming a fine precipitate or compound with other alloy elements such as P. If the Ni content is less than 0.1%, even by an optimal production method, the absolute amount of a fine Ni compound of 0.1 μm or less or of Ni contained as a solid solution becomes insufficient. Accordingly, a content of 0.1% or more is necessary for effectively bringing out those effects ofNi.

[0200] However, ifNi is excessively contained to exceed 3.0%, a compound such as oxide, crystallized product or precipitate ofNi is coarsened or a coarse Ni compound increases, as a result, the amount of a fine Ni compound or the amount ofNi contained as a solid solution rather decreases. The coarsened Ni compound becomes a starting point of fracture and leads to reduction in the strength or bendability. Accordingly, the Ni content is specified to be 0.1 to 3.0%, preferably 0.3 to 2.0%.

(Sn)

[0201] Sn is contained as a solid solution in the copper alloy matrix and thereby enhances the strength. Also, Sn contained as a solid solution suppresses the softening due to recrystallization during annealing. If the Sn content is less than 0.01%, the amount of Sn is too small and the strength cannot be enhanced, whereas if the Sn content exceeds 3.0%, not only the electrical conductivity is significantly decreased but also Sn contained as a solid solution is segregated in the grain boundary to reduce the strength or bendability. Accordingly, the Sn content is specified to be 0.01 to 3.0%, preferably 0.1 to 2.0%.

(P)

[0202] P is an element necessary for enhancing the strength or stress relaxation resistance characteristic by forming a fine precipitate with Ni. Also, P acts as a deoxidizing agent. A content of less than 0.01% causes shortage in the P-based fine precipitate particle and therefore, a content of 0.01% or more is necessary. However, if this element is excessively contained to exceed 0.3%, an Ni-P intermetallic compound precipitated particle is coarsened, which leads to reduction not only in the strength or stress relaxation resistance characteristic but also in the hot workability. Accordingly, the P content is specified to be 0.01 to 0.3%, preferably 0.02 to 0.2%.

(Fe, Zn, Mn, Si and Mg)

[0203] Fe, Zn, Mn, Si and Mg are impurities that readily intermix from a molten raw material such as scrap. These elements each produces an effect when contained but generally decreases the electrical conductivity. Also, if the content is increased, ingot making in a shaft furnace becomes difficult. Accordingly, in the case of obtaining a high electrical conductivity, the contents are specified to be 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg. In other words, the contents lower than these upper limits are allowable in the fourth embodiment of the present invention.

[0204] Fe elevates the recrystallization temperature of the copper alloy, similarly to Sn. However, if its content exceeds 0.5%, the electrical conductivity decreases. The content is preferably 0.3% or less.

[0205] Zn prevents separation of tin plating. However, if its content exceeds 1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, in the case of ingot making in a shaft furnace, the content is preferably 0.05% or less. In the temperature region (from about 150 to 180°C) where the alloy sheet is used as an automotive terminal, the effect of preventing separation of tin plating can be obtained even with a content of 0.05% or less.

[0206] Mn and Si have an effect as a deoxidizing agent. However, if the content thereof exceeds 0.1%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the contents are preferably 0.001% or less of Mn and 0.002% or less of Si.

[0207] Mg has an activity of enhancing the stress relaxation resistance characteristic. However, if its content exceeds 0.3%, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. In the case of ingot making in a shaft furnace, the content is preferably 0.001% or less.

(Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt)

[0208] The copper alloy according to the fourth embodiment of the present invention is allowed to further contain at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in an amount of 1.0% or less in terms of a total amount of these elements. These elements have an activity of preventing coarsening of the grain but, if the amount of these elements exceeds 1.0% in total, the electrical conductivity decreases and a high electrical conductivity cannot be obtained. Also, ingot making in a shaft furnace becomes difficult.

[0209] In addition, Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal are also impurities, and the amount of these elements is preferably limited to 0.1% or less in total.

(Production Method of Copper Alloy Sheet)

[0210] The production method of the copper alloy sheet according to the fourth embodiment of the present invention is described below. In producing the copper alloy sheet according to the fourth embodiment of the present invention, the production method itself may be an ordinary method except for the conditions in the finish annealing step. That is, a molten copper alloy after adjusting the component composition is subjected to casting, ingot scalping, soaking and hot rolling and then repeatedly to cold rolling and annealing, whereby a final (product) sheet is obtained. However, preferred production conditions are present for allowing the copper alloy sheet according to the fourth embodiment of the present invention to obtain necessary properties such as strength, stress relaxation resistance characteristic and press punchability, and these are described below. Also, in order to introduce a dislocation density in not less than a given amount with respect to the half-value breadth of the X-ray diffraction intensity peak, which is specified in the fourth embodiment of the present invention, it is necessary to control the conditions in the final cold rolling as described later.

[0211] In casting the above-described copper alloy composition according to the fourth embodiment of the present invention, high-productivity ingot making in a shaft furnace which is a large-scale melting furnace is possible. However, the time required is preferably as short as possible, such that the time required from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace is within 1,200 seconds and further, the time required from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling is within 1,200 seconds.

[0212] By virtue of shortening the time from the completion of addition of alloy elements to the initiation of casting in the copper alloy melting furnace and shortening the time from the extraction of ingot out of the ingot heating furnace to the completion of hot rolling, generation of a coarse Ni compound can be suppressed and at the same time, the amount of a fine Ni compound or the amount of Ni contained as a solid solution can be ensured. As a result, the copper alloy sheet can be assured of the electrical conductivity, stress relaxation resistance characteristic and strength.

[0213] Incidentally, even when it is intended to control the amount of a fine Ni compound or the amount ofNi contained as a solid solution mainly by the cold rolling conditions or annealing conditions in the later stage, the absolute amount of a fine Ni compound or ofNi contained as a solid solution already becomes small in the previous steps until the completion of hot rolling. Furthermore, in the case where the amount of a coarse Ni compound produced in the previous steps above is large, a fine product precipitated in the cold rolling and annealing steps is trapped by the coarse product and the amount of a fine product independently present in the matrix is more and more reduced. Accordingly, despite the large amount ofNi added, sufficiently high strength and excellent stress relaxation resistance characteristic may not be obtained.

[0214] Hot rolling may be performed in an ordinary manner. The inlet-side temperature of hot rolling is approximately from 600 to 1,000°C, and the finishing temperature is approximately from 600 to 850°C. After the hot rolling, water cooling or standing to cool is performed.

[0215] Thereafter, cold rolling and annealing are repeatedly performed to obtain a copper alloy sheet having a product sheet thickness. The annealing and cold rolling may be repeated according to the final (product) sheet thickness. In the cold rolling, the working ratio is selected so that a working ratio of approximately from 30 to 80% can be obtained in the final finish rolling. In the middle of the cold rolling, intermediate recrystallization annealing may be appropriately interposed.

(Final Cold Rolling)

[0216] In order to introduce a dislocation density in not less than a given amount such that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the copper alloy sheet surface by the peak height is 1.0×10^{-4} or more, the strain amount introduced in the final cold rolling is increased. That is, after setting the roll length (roll width) in the final cold rolling to 500 mm or more, a technique such as use of a small-size roll having a roll diameter of less than 80 mmϕ or setting of the minimum rolling reduction (cold rolling ratio, working ratio) per pass to 20% or more is selected and used, or these techniques are used in combination.

[0217] If the roll diameter in the final cold rolling is too small, if the minimum rolling reduction per pass is too small or if the roll length is too short, there is a high possibility that the dislocation density introduced into the copper alloy sheet is insufficient. As a result, the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface by the peak height becomes less than 1.0×10^{-4}, making little difference from the conventional copper alloy sheet with a small dislocation density, and the stress relaxation resistance characteristic and press punchability are decreased or not enhanced.

[0218] As for the number of passes in the final cold rolling, the rolling is preferably performed usually in 3 or 4 passes while avoiding an excessively small or large number of passes. Also, the rolling reduction per pass need not exceed 50% and each rolling reduction per pass is determined by taking into consideration the original sheet thickness, final sheet thickness after cold rolling, number of passes, minimum rolling reduction per pass, and maximum rolling reduction.

(Final Annealing)

[0219] In the finish annealing, as for the finish annealing temperature, the finish annealing is preferably performed at a maximum peak temperature of 500 to 800°C in terms of the substantial temperature of the sheet, and the holding time in this temperature range is preferably from 10 to 60 seconds.

[0220] The strain relief annealing or stabilizing annealing after the final finish cold rolling is preferably performed under the conditions of a substantial temperature of 250 to 450°C x 20 to 40 seconds. By this annealing, the strain introduced in the final finish rolling can be removed. At the same time, softening of the material does not occur and reduction in the strength can be suppressed.

Examples

(1) First Example (Example According to First Embodiment of the Present Invention)

[0221] Working examples according to the first embodiment of the present invention are described below. Copper alloy thin sheets were produced using various Cu-Ni-Sn-P-based alloys by varying the composition and finish annealing conditions (continuous annealing) and evaluated for various properties such as electrical conductivity, strength, elongation and stress relaxation resistance characteristic.

[0222] More specifically, a copper alloy having a chemical component composition shown in Table 1 was melted in a coreless furnace and then subjected to ingot making by a semicontinuous casting method (cold solidification rate of casting: 2°C/sec) to obtain an ingot of 70 mm (thickness) x 200 mm (width) x 500 mm (length). The obtained ingots were rolled in common under the following conditions to obtain a copper alloy thin sheet. After the surface of each ingot was scalped and heated, the ingot was heated at 960°C in a heating furnace and immediately hot-rolled at a hot rolling finishing temperature of 750°C into a 16 mm-thick sheet, and the sheet was quenched in water from a temperature of 650°C or more.

[0223] In this process, the time required from the completion of addition of alloy elements to the initiation of casting in the melting furnace was set to 1,200 seconds or less commonly among respective Examples, and the time required from the extraction out of the heating furnace to the completion of hot rolling was set to 1,200 seconds or less commonly among respective Examples.

[0224] After the removal of oxide scales, the sheet was subjected to cold rolling, continuous finish annealing, cold rolling, and strain relief annealing in this order to produce a copper alloy thin sheet. That is, the sheet after primary cold rolling (rough cold rolling, intermediate cold rolling) was scalped. Finish annealing of the sheet was performed in an annealing furnace at the average temperature rise rate, maximum peak temperature and average cooling rate from 400°C to room temperature each shown in Table 2. Incidentally, the cooling from the maximum peak temperature to 400°C was quenching at an average cooling rate of 100°C/s. Also, commonly in respective Examples, the sheet was held at the maximum peak temperature for 20 seconds.

[0225] After the finish annealing, finish cold rolling at a rolling reduction of 60% and then, low-temperature strain relief annealing under the conditions of a substantial temperature of 400°C for 20 seconds were performed to obtain a 0.25 mm-thick copper alloy thin sheet.

(X-Ray Diffraction Pattern)

[0226] A test specimen was sampled from each of the thus-obtained copper alloy thin sheets and after the X-ray diffraction pattern of the test specimen surface was measured by an X-ray diffraction analyzer (Model: RINT 1500) manufactured by Rigaku Corporation, the presence or absence of an intensity peak at the X-ray diffraction angle (2θ) between 100° and 102° (in the vicinity of 101°) in the obtained X-ray diffraction pattern was determined. The scan rate was 2°/min and the sampling width was 0.02°.

[0227] Incidentally, when it was recognized that an intensity peak rising over fluctuation (variation) of the intensity peak due to noise was substantially present at the X-ray diffraction angle between 100° and 102°, the intensity peak was judged as being present. On the contrary, when it was recognized that only fluctuation (variation) of the intensity peak due to noise was present between those X-ray diffraction angles, the intensity peak was judged as being not present. The results obtained are shown in Table 2.

[0228] Also, in each of Examples, a sample was cut out from the obtained copper alloy sheet and subjected to electrical conductivity measurement, tensile test and stress relaxation ratio measurement. The results obtained are also shown in Table 2.

(Tensile Test)

[0229] A test specimen was sampled from the copper alloy thin sheet and machined to produce a JIS No. 5 tensile test specimen such that the longitudinal direction of the test specimen runs in the direction orthogonal to the rolling direction of the sheet material. This test specimen was measured for mechanical properties including elongation under the conditions of room temperature, a test speed of 10.0 mm/min and GL = 50 mm by a universal tester Model 5882 manufactured by Instron Corp. Incidentally, the proof stress is tensile strength corresponding to a permanent elongation of 0.2%.

(Electrical Conductivity Measurement)

[0230] A sample was extracted from the copper alloy thin sheet and measured for the electrical conductivity. In measuring the electrical conductivity of the copper alloy sheet sample, the sheet was worked into a strip-like test specimen of 10 mm (width) x 300 mm (length) by milling and measured for the electrical resistance by a double bridge-type resistance measuring apparatus according to the measuring method of electrical conductivity of nonferrous metal materials specified in JIS-H0505, and the electrical conductivity was calculated according to the average cross-sectional area method.

(Stress Relaxation Characteristic)

[0231] The copper alloy thin sheet was evaluated for the stress relaxation resistance characteristic in the direction parallel to the rolling direction by measuring the stress relaxation ratio in this direction. More specifically, a test specimen was sampled from the copper alloy thin sheet and measured using the cantilever system shown in Fig. 3. A 10 mm-wide strip-like specimen 1 (with the length direction running in the direction parallel to the rolling direction of the sheet material) was cut out and fixed at one end to a rigid test board 2, and deflection in a size of d (= 10 mm) was given to the portion in a span length L of the specimen 1. At this time, L was determined such that a surface stress corresponding to 80% of the proof stress of the material was loaded on the material. After holding in an oven at 180°C for 30 hours, the specimen was taken out, and the permanent distortion δ after removing the deflection d was determined. The stress relaxation ratio (RS) was calculated according to the formula: $RS = (\delta/d) \times 100$. Incidentally, holding of 180°C × 30 hours corresponds to holding of almost 150°C × 1,000 hours as calculated using the Larson-Miller parameter.

[0232] As apparent from Table 2, in Inventive Examples 1 to 13 using a copper alloy within the composition range of the first embodiment of the present invention in Table 1 (alloy Nos. 1 to 10), the copper alloy sheets are produced within preferred conditions in terms of the average temperature rise rate of finish annealing and the average cooling rate, particularly, from 400°C to room temperature. Also, the heating furnace extraction temperature and the hot rolling finishing temperature are appropriate. Furthermore, the time required from the completion of addition of alloy elements to the initiation of casting in the melting furnace and the time required from the extraction out of the heating furnace to the completion of hot rolling are also short and proper.

[0233] Accordingly, in Inventive Examples of Table 2, an intensity peak (the specific intensity peak a in Figs. 1 and 2) is present at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern above. Incidentally, Figs. 1 and 2 show the X-ray diffraction pattern of only Inventive Example 1, but in other Inventive Examples, similarly to Inventive Example 1, the specific intensity peak denoted by the arrow a is present at the X-ray diffraction angle (2θ) between 100° and 102°.

[0234] In addition, it is presumed that since the copper alloy sheets of Inventive Examples are produced within the above-described preferred conditions, production of a coarse Ni compound such as oxide, crystallized product or precipitate ofNi is suppressed and the amount of a fine Ni compound or the like or the amount ofNi contained as a solid solution can be ensured.

[0235] As a result, the copper alloy sheets of Inventive Examples have, as terminal/connector properties, an electrical conductivity of 32% IACS or more and a stress relaxation ratio in the direction parallel to the rolling direction of 15% or less and further has, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and an elongation of 10% or more. That is, the copper alloy sheets of Inventive Examples are assured particularly of high elongation, strength and electrical conductivity and excellent in the balance of electrical conductivity and strength with ductility and also fulfill the standard for the stress relaxation resistance characteristic, revealing that the copper alloy sheet satisfies all of these properties at the same time.

[0236] Accordingly, these Inventive Examples have high formability allowing for bending work even in a high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector, which requires bending conditions in a high-speed deformation region with a large strain rate.

[0237] However, out of Inventive Examples of Table 2, in both of Inventive Example 2 where the average temperature rise rate of finish annealing is the lower limit of 50°C/s and relatively slow, and Inventive Example 3 where the average cooling rate from 400° to room temperature is the lower limit of 40°C/h and relatively slow, the strength, elongation and stress relaxation resistance characteristic all are relatively lower than those in Inventive Examples 1 and 5 where those conditions are appropriate. Also, in Inventive Example 4 where the average cooling rate from 400°C to room temperature is the upper limit of 100°C/h and relatively fast, the elongation in particular is relatively lower than that in Inventive Examples 1 and 5 where the condition above is appropriate.

[0238] Also, out of Inventive Examples of Table 2, in Inventive Examples 12 and 13 (alloy Nos. 9 and 10 of Table 1) where the amount of other elements exceeds the preferred upper limit, the electrical conductivity is reduced as compared with other Inventive Examples where the electrical conductivity is relatively high. In Inventive Example 12, as shown in alloy No. 9 of Table 1, the total of elements in Element Group A: Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt is high to exceed the preferred upper limit of 1.0 mass%. In Inventive Example 13, as shown in alloy No. 10 of Table 1, the total of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal is high to exceed the preferred upper limit of 0.1 mass%.

[0239] In Inventive Example 6 of Table 2 (alloy No. 3 of Table 1), the Ni content is the lower limit of 0.1%; in Inventive Example 7 (alloy No. 4 of Table 1), the Ni content is the upper limit of 3.0%; in Inventive Example 8 (alloy No. 5 of Table 1), the Sn content is the lower limit of 0.01%; in Inventive Example 9 (alloy No. 6 of Table 1), the Sn content is the upper limit of 3.0%; in Inventive Example 10 (alloy No. 7 of Table 1), the P content is the lower limit of 0.01%; and in Inventive Example 11 (alloy No. 8 of Table 1), the P content is the upper limit of 0.3%.

[0240] Accordingly, in Inventive Examples 6, 8 and 10 of Table 2 where the amount of the main alloy element is the lower limit, particularly, the stress relaxation resistance characteristic and strength are relatively low as compared with Inventive Examples 1 and 5 where the amount of the main alloy element is appropriate. Also, in Inventive Examples 7, 9 and 11 where the amount of the main alloy element is the upper limit, the electrical conductivity, stress relaxation resistance characteristic and elongation are relatively low as compared with Inventive Examples 1 and 5 where the amount of the main alloy element is appropriate.

[0241] In Comparative Examples 14 to 19 of Table 2, the production conditions such as finish annealing are within the preferred range and therefore, similarly to Inventive Examples, the intensity peak (the specific intensity peak a in Figs. 1 and 2) at the X-ray diffraction angle (2θ) between 100° and 102° in the X-ray diffraction pattern is present. Nevertheless, due to use of alloy Nos. 11 to 16 of Table 1 which are a copper alloy out of the composition range of the first embodiment of the present invention, any one of the electrical conductivity, stress relaxation resistance characteristic, strength and elongation is significantly inferior to Inventive Examples.

[0242] In Comparative Example 14, the Ni content deviates below the lower limit (alloy No. 11 of Table 1) and therefore, the strength, stress relaxation resistance characteristic and elongation are low. In Comparative Example 15, the Ni content deviates above the upper limit (alloy No. 12 of Table 1) and therefore, the strength, stress relaxation resistance characteristic and elongation are low.

[0243] In Comparative Example 16, the Sn content deviates below the lower limit (alloy No. 13 of Table 1). Therefore, in Comparative Example 16, the strength, elongation and stress relaxation resistance characteristic are excessively low. In the copper alloy of Comparative Example 17, the Sn content deviates above the upper limit (alloy No. 14 of Table 1) and therefore, the electrical conductivity and elongation are low.

[0244] In Comparative Example 18, the P content deviates below the lower limit (alloy No. 15 of Table 1) and therefore, the strength, elongation and stress relaxation resistance characteristic are low. In Comparative Example 19, the P content deviates above the upper limit (alloy No. 16 of Table 1) and therefore, cracking occurred during hot rolling, failing in characterization.

[0245] In Comparative Examples 20 to 24 of Table 2, a copper alloy within the composition range of the first embodiment of the present invention in Table 1 is used (alloy Nos. 1 and 2) and other production conditions are within the preferred range, similarly to Inventive Examples. Nevertheless, only the conditions of the finish annealing are out of the preferred range. In Comparative Example 20, the average temperature rise rate of finish annealing is less than the lower limit and is too slow; in Comparative Examples 21 and 22, the average cooling rate from 400°C to room temperature exceeds the upper limit and is too fast; and in Comparative Examples 23 and 24, the average cooling rate from 400°C to room temperature is less than the lower limit and is too slow.

[0246] As a result, in Comparative Examples 20 to 24, unlike Inventive Examples, a specific intensity peak a shown in Fig. 1 is not present at the X-ray diffraction angle (2θ) between 100° and 102°. Accordingly, in these Comparative Examples, all of the electrical conductivity, strength and elongation in particular are extremely inferior to Inventive Examples, though the stress relaxation resistance characteristic is rather equal to that in Inventive Examples.

[0247] These results reinforce the meanings of the component composition of the copper alloy in the first embodiment of the present invention and the X-ray diffraction pattern, for obtaining a Cu-Ni-Sn-P-based alloy sheet with excellent strength-ductility balance, which is responsive to the high-efficiency high-speed press forming process subject to working conditions in a high-speed deformation region with a large strain rate and satisfies also the properties required for a terminal or connector, and further the meanings of the preferred production conditions for obtaining the X-ray diffraction pattern above.

[0248] That is, in the first embodiment of the present invention, a novel Cu-Ni-Sn-P-based alloy sheet having, even when the 0.2%-proof stress is 500 MPa or more, an elongation of 10% or more, an electrical conductivity of 32% IACS or more and a stress relaxation ratio of 15% or less is obtained. As more excellent properties, a Cu-Ni-Sn-P-based alloy sheet having an electrical conductivity of 35% IACS or more, a stress relaxation ratio of 15% or less, a 0.2%-proof stress of 520 MPa or more and an elongation of 12% or more is obtained.

Table 1

Class	No.	Chemical Component Composition of Copper Alloy Sheet (balance: Cu)									
		Ni	Sn	P	Fe	Zn	Mn	Si	Mg	Element Group A	Element Group B
Inventive Example	1	0.8	1.1	0.07	0.02	0.04	-	-	-	-	-
	2	1.1	0.8	0.06	0.02	-	0.01	-	0.01	-	-
	3	0.1	1.1	0.07	0.02	0.04	-	-	-	-	-
	4	3.0	1.1	0.07	0.02	0.04	-	-	-	-	-
	5	1.1	0.01	0.06	0.02	-	0.01	-	0.01	-	-
	6	0.5	3.0	0.04	0.02	-	0.01	-	0.01	-	-
	7	1.1	0.8	0.01	0.02	-	0.01	-	0.01	-	-
	8	1.1	0.8	0.3	0.02	-	0.01	-	0.01	-	-
	9	0.8	1.1	0.07	0.02	0.04	-	-	-	1.1	-
	10	0.8	1.1	0.07	0.02	0.04	-	-	-	-	0.2
Comparative Example	11	0.04	1.1	0.07	0.02	0.04	-	-	-	-	-
	12	3.1	1.1	0.07	0.02	0.04	-	-	-	-	-
	13	0.8	-	0.07	0.02	0.04	-	-	-	-	-
	14	0.8	3.1	0.07	0.02	0.04	-	-	-	-	-
	15	0.80	1.1	0.004	0.02	0.04	-	-	-	-	-
	16	0.80	1.1	0.35	0.02	0.04	-	-	-	-	-

* "-" indicates that the content is below the detection limit.
* Other Element Group A: the total content of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt.
* Other Element Group B: the total content of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal.

Table 2

Class	No.	Alloy No. of Table 1	Finish Annealing Conditions			X-Ray Diffraction Pattern	Properties of Copper Alloy Sheet				
			Average Temperature Rise Rate (°C/s)	Maximum Peak Temperature (°C)	Average Cooling Rate from 400°C (°C/h)	Presence or Absence of Intensity Peak Near 101°	Electrical Conductivity (%IACS)	Tensile Strength (MPa)	0.2%-Proof Stress (MPa)	Elongation (%)	Stress Relaxation Ratio (%)
Inventive Example	1	1	200	660	70	present	40	600	580	13	11
	2	1	50	660	70	present	41	590	575	12	13
	3	1	200	660	40	present	42	585	570	12	13
	4	1	200	660	100	present	39	610	590	11	14
	5	2	100	660	50	present	43	535	520	14	13
	6	3	150	600	70	present	40	515	500	15	15
	7	4	220	550	70	present	35	600	585	12	10
	8	5	200	700	70	present	45	515	500	14	13
	9	6	200	660	70	present	30	660	645	10	12
	10	7	200	660	70	present	44	550	535	13	14
	11	8	200	660	70	present	35	620	605	12	13
	12	9	200	660	70	present	38	630	610	12	11
	13	10	200	660	70	present	39	605	585	13	13
Comparative Example	14	11	200	660	70	present	38	495	480	9	18
	15	12	200	660	70	present	32	580	560	7	15
	16	13	200	660	70	present	47	500	480	8	15
	17	14	200	660	70	present	28	665	650	7	12
	18	15	200	660	70	present	45	535	515	9	16
	19	16	200	660	70	present	-	-	-	-	-
	20	1	30	660	70	none	41	580	565	6	13
	21	1	200	660	120	none	37	570	550	7	12
	22	1	200	660	150	none	35	550	535	7	11
	23	1	200	660	20	none	42	530	515	7	13
	24	2	200	660	30	none	43	520	505	8	14

(2) Second Example (Example According to Second Embodiment of the Present Invention)

[0249] Working examples according to the second embodiment of the present invention are described below. Copper alloy thin sheets varied in the X-ray diffraction intensity ratio I(200)/I(220) by controlling the rolling speed in the final cold rolling and the sheet passage rate and annealing temperature at the low-temperature final annealing in a continuous heat-treating furnace after the final cold rolling. These copper alloy thin sheets each was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress and stress relaxation resistance characteristic.

[0250] More specifically, a copper alloy having a chemical component composition shown in Table 3 (the balance of the composition excluding the element amounts shown is Cu) was melted in a coreless furnace and then subjected to ingot making by a semicontinuous casting method (cold solidification rate of casting: 2°C/sec) to produce an ingot of 70 mm (thickness) × 200 mm (width) × 500 mm (length). The obtained ingots were rolled in common under the following conditions to obtain a copper alloy thin sheet. After the surface of each ingot was scalped and heated, the ingot was heated at 960°C in a heating furnace and immediately hot-rolled at a hot rolling finishing temperature of 750°C into a 16 mm-thick sheet, and the sheet was quenched in water from a temperature of 650°C or more.

[0251] In this process, the time required from the completion of addition of alloy elements to the initiation of casting in the melting furnace was set to 1,200 seconds or less commonly among respective Examples, and the time required from the extraction out of the heating furnace to the completion of hot rolling was set to 1,200 seconds or less commonly among respective Examples.

[0252] After the removal of oxide scales, the sheet was subjected to cold rolling, continuous finish annealing, cold rolling and strain relief annealing in this order to produce a copper alloy thin sheet. That is, the sheet after primary cold rolling (rough cold rolling, intermediate cold rolling) was scalped. Finish annealing of the sheet was performed in an annealing furnace at the maximum peak temperature of 600°C in terms of the substantial temperature of the sheet by holding the sheet at this temperature for 60 seconds.

[0253] After the finish annealing, final cold rolling at a rolling reduction of 60% was performed. The rolling speed in this final cold rolling was controlled. Incidentally, a roll having the same roll diameter (60 mm) and roll length (500 mm) was used in all of 4 passes of the final cold rolling, and the rolling reduction per pass was also made the same at 30%.

[0254] After the final cold rolling, low-temperature annealing was performed in a continuous annealing furnace by making constant the substantial temperature (maximum peak temperature) at 350°C and varying the sheet passage rate as shown in Table 4 to obtain a 0.25 mm-thick copper alloy thin sheet.

[0255] In all of the copper alloys shown in Table 3, the balance of the composition excluding the element amounts shown is Cu, and the content of elements of Group A, that is, Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, as other impurity elements was 1.0 mass% or less in total of these elements, except for Inventive Example 25 of Table 3 (Inventive Example 34 of Table 4).

[0256] Also, the content of elements of Group B, that is, Hf, Th, Li, Na, K, Sr, Pd, W, S, Si, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, was 0.1 mass% or less in total of these elements, except for Inventive Example 26 of Table 3 (Inventive Example 35 of Table 4).

[0257] In each of Examples, a sample was cut out from the obtained copper alloy sheet, and the sample was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress and stress relaxation resistance characteristic. The results obtained are shown in Table 4.

(Measurement of Texture)

[0258] With respect to the copper alloy sheet sample, the X-ray diffraction intensity I(200) from (200) plane in the sheet surface and the X-ray diffraction intensity I(220) from (220) plane were measured under the conditions of a tube voltage of 40 kV, a tube current of 200 mA, a scan rate of 2°/min, a sampling width of 0.02° and a measurement range (2θ) of 30 to 115° by using an X-ray diffraction analyzer (Model: RINT 1500) manufactured by Rigaku Corporation and using Co as the target, and the X-ray diffraction intensity ratio I(200)/I(220) was determined. The measurement was performed at two portions and an average of the values obtained was used as I(200)/I(220).

(Measurement of Average grain size)

[0259] The average grain size was measured by a crystal orientation analysis method using FESEM/EBSP described above. The measured portion of the test specimen was in common arbitrary 5 portions, the measured values as the average particle grain size of these 5 portions were averaged, and the obtained value was used for the average crystal grain size.

(Tensile Test)

[0260] A test specimen was sampled from the copper alloy thin sheet and machined to produce a JIS No. 5 tensile test specimen such that the longitudinal direction of the test specimen runs in the direction orthogonal to the rolling direction of the sheet material. This test specimen was measured for mechanical properties including elongation under the conditions of room temperature, a test speed of 10.0 mm/min and GL = 50 mm by a universal tester Model 5882 manufactured by Instron Corp. Incidentally, the proof stress is tensile strength corresponding to a permanent elongation of 0.2%.

(Measurement of Electrical Conductivity)

[0261] A sample was extracted from the copper alloy thin sheet and measured for the electrical conductivity. In measuring the electrical conductivity of the copper alloy sheet sample, the sheet was worked into a strip-like test specimen of 10 mm (width) × 300 mm (length) by milling and measured for the electrical resistance by a double bridge-type resistance measuring apparatus according to the measuring method of electrical conductivity of nonferrous metal materials specified in JIS-H0505, and the electrical conductivity was calculated according to the average cross-sectional area method.

(Stress Relaxation Characteristic)

[0262] The copper alloy thin sheet was evaluated for the stress relaxation resistance characteristic in each of the parallel direction and the orthogonal direction involving severer stress relaxation than in the parallel direction, with respect to the rolling direction by measuring the stress relaxation ratio in these directions. In the stress relaxation ratio measuring test below, a sample where the stress relaxation ratio is less than 10% in both the parallel direction and the orthogonal direction with respect to the rolling direction and the difference in the stress relaxation ratio between the parallel direction and the orthogonal direction is within 3% is judged as passed in terms of the stress relaxation resistance characteristic.

[0263] More specifically, in the measurement of the stress relaxation ratio, a test specimen was sampled from the copper alloy thin sheet and measured using the cantilever system shown in Fig. 3. A 10 mm-wide strip-like specimen 1 (with the length direction running in the direction orthogonal to the rolling direction of the sheet material) was cut out and fixed at one end to a rigid test board 2, and deflection in a size of d (= 10 mm) was given to the portion in a span length L of the specimen 1. At this time, L was determined such that a surface stress corresponding to 80% of the proof stress of the material was loaded on the material. After holding in an oven at 120°C for 3,000 hours, the specimen was taken out, and the permanent distortion δ after removing the deflection d was determined. The stress relaxation ratio (RS) was calculated according to the formula: $RS = (\delta/d) \times 100$.

[0264] As apparent from Table 4, in Inventive Examples 25 to 35 using a copper alloy within the composition range of the second embodiment of the present invention in Table 3 (alloy Nos. 17 to 26), the copper alloy sheets are produced within preferred conditions of the production method such as rolling speed in final cold rolling and sheet passage rate in final annealing. Accordingly, in Inventive Examples of Table 4, the X-ray diffraction intensity ratio I(200)/I(220) in the surface of the Cu-Ni-Sn-P-based copper alloy sheet is 0.25 or less. Also, the average grain size was as fine as 5.0 μm or less.

[0265] In addition, it is presumed that since the copper alloy sheets of Inventive Examples have a composition in an appropriate range and are produced within the above-described preferred conditions, production of a coarse Ni compound such as oxide, crystallized product or precipitate ofNi is suppressed and the amount of a fine Ni compound or the like or the amount ofNi contained as a solid solution can be ensured.

[0266] As a result, the copper alloy sheets of Inventive Examples 25 to 33 of Table 4 have, as terminal/connector properties, an electrical conductivity of 30% IACS or more and a stress relaxation ratio of less than 10% in the orthogonal direction involving severer stress relaxation, with respect to the rolling direction. The difference in the stress relaxation ratio between the orthogonal direction and the parallel direction with respect to the rolling direction is also as small as approximately from about 2 to 3%. Moreover, the copper alloy sheet further has, as mechanical properties, a 0.2%-proof stress of 500 MPa or more. That is, the copper alloy sheets of Inventive Examples are assured of high electrical conductivity and strength and excellent particularly in the stress relaxation resistance characteristic, revealing that the copper alloy sheet satisfies all of these properties at the same time.

[0267] However, out of Inventive Examples of Table 4, in Inventive Examples 34 and 35 (alloy Nos. 25 and 26 of Table 3) where the amount of other elements exceeds the preferred upper limit, the electrical conductivity is reduced as compared with other Inventive Examples where the electrical conductivity is relatively high. In Inventive Example 34, as shown in alloy No. 25 of Table 3, the total of elements in Element Group A: Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt is high to exceed the preferred upper limit of 1.0 mass%. In Inventive Example 35, as shown in alloy No. 26 of Table 3, the total of elements in Element Group B: Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal is high to exceed the preferred upper limit of 0.1 mass%.

[0268] In Inventive Example 28 of Table 4 (alloy No. 19 of Table 3), the Ni content is the lower limit of 0.1%; in Inventive Example 29 (alloy No. 20 of Table 3), the Ni content is the upper limit of 3.0%; in Inventive Example 30 (alloy No. 21 of Table 3), the Sn content is the lower limit of 0.01%; in Inventive Example 31 (alloy No. 22 of Table 3), the Sn content is the upper limit of 3.0%; in Inventive Example 32 (alloy No. 23 of Table 3), the P content is the lower limit of 0.01%; and in Inventive Example 33 (alloy No. 24 of Table 3), the P content is the upper limit of 0.3%.

[0269] Also, in Inventive Example 26 of Table 4 where the production conditions such as rolling speed in final cold rolling and sheet passage rate in final annealing are on the lower limit side, the stress relaxation resistance characteristic and strength are relatively lower than those in Inventive Example 25.

[0270] In Comparative Examples 36 to 41 of Table 4, the copper alloy sheets are produced within preferred conditions of the production method such as rolling speed in final cold rolling and sheet passage rate in final annealing. Accordingly, in Comparative Examples 36 to 41, the copper alloy sheet has anisotropy that the X-ray diffraction intensity ratio I(200) /I(220) in the surface of the Cu-Ni-Sn-P-based copper alloy sheet is 0.25 or less. Nevertheless, in these Comparative Examples, due to use of alloy Nos. 27 to 32 of Table 3 which are a copper alloy out of the composition range of the second embodiment of the present invention, any one of the electrical conductivity, strength and stress relaxation resistance characteristic is significantly inferior to Inventive Examples.

[0271] In Comparative Example 36 of Table 4, the Ni content deviates below the lower limit (alloy No. 27 of Table 3) and therefore, the strength and stress relaxation resistance characteristic are low. In Comparative Example 37, the Ni content deviates above the upper limit (alloy No. 28 of Table 3) and therefore, the balance between strength and electrical conductivity is low.

[0272] In Comparative Example 38, the Sn content deviates below the lower limit (alloy No. 29 of Table 3) and therefore, the strength and stress relaxation resistance characteristic are excessively low. In the copper alloy of Comparative Example 39, the Sn content deviates above the upper limit (alloy No. 30 of Table 3) and therefore, the electrical conductivity is low.

[0273] In Comparative Example 40, the P content deviates below the lower limit (alloy No. 31 of Table 3) and therefore, the strength and stress relaxation resistance characteristic are low. In Comparative Example 41, the P content deviates above the upper limit (alloy No. 32 of Table 3) and therefore, cracking occurred during hot rolling, failing in characterization.

[0274] In Comparative Examples 42 and 43 of Table 4, a copper alloy within the composition range of the second embodiment of the present invention in Table 3 is used (alloy Nos. 17 and 18) and other production conditions are also within the preferred range, similarly to Inventive Examples. Nevertheless, the rolling speed in final cold rolling or the sheet passage rate in final annealing are out of the preferred range. In Comparative Example 42, the rolling speed in final cold rolling is too slow, and in Comparative Example 43, the rolling speed in final cold rolling is too low and at the same time, the sheet passage rate in final annealing is too slow.

[0275] As a result, in Comparative Examples 42 and 43, the X-ray diffraction intensity ratio I(200)/I(220) in the surface of the Cu-Ni-Sn-P-based copper alloy sheet exceeds 0.25. Also, the average grain size is coarsened to exceed 5.0 μm. Accordingly, in these Comparative Examples, the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction is extremely inferior to Inventive Examples. Furthermore, the difference between the stress relaxation ratio in the direction orthogonal to the rolling direction and the stress relaxation ratio in the direction parallel to the rolling direction is large. In addition, the strength is low as compared with Inventive Examples.

[0276] These results reinforce the meanings of the component composition and texture of the copper alloy in the second embodiment of the present invention for obtaining a Cu-Ni-Sn-P-based alloy sheet satisfying the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction, creating not so much difference from the stress relaxation resistance characteristic in the direction parallel to the rolling direction, and being excellent also in other properties required for a terminal or a connector, and further the meaning of the preferred production conditions for obtaining the texture.

Table 3

Class	No.	Chemical Component Composition of Copper Alloy Sheet (balance: Cu)									
		Ni	Sn	P	Fe	Zn	Mn	Si	Mg	Element Group A, #	Element Group B, #
Inventive Example	17	0.9	1.1	0.08	0.02	0.04	-	-	-	-	-
	18	1.1	0.7	0.06	0.02	0.01	-	-	0.01	-	-
	19	0.1	1.0	0.08	0.02	0.03	0.01	-	0.01	-	-
	20	3.0	1.0	0.08	0.02	0.03	-	0.01	-	-	-
	21	0.9	0.01	0.08	0.02	-	-	0.01	-	-	-
	22	0.6	3.0	0.04	0.02	-	0.01		-	-	-
	23	1.1	0.7	0.01	0.02	0.04	-	-	0.01	-	-
	24	1.1	0.7	0.3	0.02	-	-	0.01	-	-	-
	25	0.9	1.0	0.08	0.02	0.03	-	-	-	1.1	-
	26	0.9	1.0	0.08	0.02	0.03	-	-	0.01	-	0.3
Comparative Example	27	0.04	1.0	0.08	0.02	-	-	-	0.01	-	-
	28	3.2	1.0	0.08	0.02	0.04	0.01	-	-	-	-
	29	0.9	-	0.08	0.02	0.04	0.01	-	-	-	-
	30	0.9	3.2	0.08	0.02	0.04	-	0.01	-	-	-
	31	0.9	1.0	0.004	0.02	0.03	0.01	0.01	-	-	-
	32	0.9	1.0	0.35	0.02	-	0.01	-	0.01	-	-

* "-" indicates that the content is below the detection limit.
* Other Element Group A: the total content of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt.
* Other Element Group B: the total content of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal.

Table 4

Class	No.	Alloy No. of Table 3	Final Cold Rolling, Rolling Speed (m/min)	Final Continuous Annealing, Sheet Passage Rate (m/min)	Properties of Copper Alloy Sheet							
					Texture		Electrical Conductivity (%IACS)	Tensile Strength (MPa)	0.2%-Proof Stress (MPa)	Stress Relaxation Ratio		
					X-Ray Diffraction Intensity Ratio I (200)/I (220)	Average grain size (µm)				Orthogonal Direction (%)	Parallel Direction (%)	Difference (%)
Inventive Example	25	17	300	500	0.17	3.0	35	590	570	7	5	2
	26	17	200	100	0.24	4.5	37	550	535	9	7	2
	27	18	300	30	0.19	4.9	38	555	540	8	6	2
	28	19	200	50	0.20	3.5	41	540	520	9	6	3
	29	20	300	30	0.16	4.2	34	595	580	8	5	3
	30	21	250	70	0.21	3.6	44	530	510	9	7	2
	31	22	300	30	0.18	3.2	31	640	620	8	6	2
	32	23	300	70	0.22	3.5	42	535	515	9	7	2
	33	24	250	30	0.20	4.0	33	625	605	9	6	3
	34	25	200	50	0.23	3.7	29	660	640	9	7	2
	35	26	200	50	0.21	3.8	30	645	625	9	7	2
Comparative Example	36	27	200	30	0.22	3.9	41	510	490	12	8	4
	37	28	300	30	0.19	4.2	32	580	560	9	6	3
	38	29	200	30	0.23	3.8	45	490	475	10	7	3
	39	30	300	10	0.20	3.1	28	615	595	9	7	2
	40	31	200	50	0.24	3.7	43	505	485	11	7	4
	41	32	-	-	-	-	-	-	-	-	-	-
	42	17	100	50	0.27	5.4	35	560	540	12	7	5
	43	18	100	5	0.29	6.8	38	540	520	13	8	5

(3) Third Example (Example According to Third Embodiment of the Present Invention)

[0277] Working examples according to the third embodiment of the present invention are described below. Copper alloy thin sheets varied in the texture with respect to a distribution density of Brass orientation and a sum of distribution densities of Brass orientation, S orientation and Copper orientation, were produced by controlling the cold rolling ratio (rolling reduction) per pass at the final cold rolling and the tension imposed on the copper alloy sheet when passing at the final annealing in a continuous heat-treating furnace. These copper alloy thin sheets each was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress, stress relaxation resistance characteristic and bendability.

[0278] More specifically, a copper alloy having a chemical component composition shown in Table 5 (the balance of the composition excluding the element amounts shown is Cu) was melted in a coreless furnace and then subjected to ingot making by a semicontinuous casting method (cold solidification rate of casting: 2°C/sec) to obtain an ingot of 70 mm (thickness) x 200 mm (width) x 500 mm (length). The obtained ingots were rolled in common under the following conditions to produce a copper alloy thin sheet. After the surface of each ingot was scalped and heated, the ingot was heated at 960°C in a heating furnace and immediately hot-rolled at a hot rolling finishing temperature of 750°C into a 16 mm-thick sheet, and the sheet was quenched in water from a temperature of 650°C or more.

[0279] In this process, the time required from the completion of addition of alloy elements to the initiation of casting in the melting furnace was set to 1,200 seconds or less commonly among respective Examples, and the time required from the extraction out of the heating furnace to the completion of hot rolling was set to 1,200 seconds or less commonly among respective Examples.

[0280] After the removal of oxide scales, the sheet was subjected to cold rolling, continuous finish annealing, cold rolling and strain relief annealing in this order to produce a copper alloy thin sheet. That is, the sheet after primary cold rolling (rough cold rolling, intermediate cold rolling) was scalped. Finish annealing of the sheet was performed in an annealing furnace at the maximum peak temperature of 600°C in terms of the substantial temperature of the sheet by holding the sheet at this temperature for 60 seconds.

[0281] After the finish annealing, final cold rolling was performed. The cold rolling ratio (rolling reduction) in this final cold rolling was controlled to the values shown in Table 6. Incidentally, a roll having the same roll diameter (60 mm) and roll length (500 mm) was used in all of 4 passes of the final cold rolling.

[0282] After the final cold rolling, low-temperature annealing was performed in a continuous annealing furnace by making constant the substantial temperature (maximum peak temperature) at 350°C and varying the tension imposed on the copper alloy sheet when passing to obtain a 0.25 mm-thick copper alloy thin sheet.

[0283] In all of the copper alloys shown in Table 5, the balance of the composition excluding the element amounts shown is Cu, and the content of elements of Group A, that is, Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, as other impurity elements was 1.0 mass% or less in total of these elements, except for Inventive Example 41 of Table 5 (Inventive Example 54 of Table 6).

[0284] Also, the content of elements of Group B, that is, Hf, Th, Li, Na, K, Sr, Pd, W, S, Si, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, was 0.1 mass% or less in total of these elements, except for Inventive Example 42 of Table 5 (Inventive Example 55 of Table 6).

[0285] In each of Examples, a sample was cut out from the obtained copper alloy sheet, and the sample was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress, stress relaxation resistance characteristic and bendability. The results obtained are shown in Table 6.

(Measurement of Texture)

[0286] A test specimen for the observation of texture was sampled from the obtained copper alloy sheet and after mechanical polishing and buff polishing, the surface was regulated by electrolytic polishing. Measurement of each of the obtained test specimens by the above-described method was performed at intervals of 1 μm with respect to a region of 500 μm × 500 μm. The measurement and analysis were performed, as described above, by using FESEM manufactured by JEOL Ltd. and the EBSP measurement/analysis system manufactured by TSL and using an analysis software for the system, whereby the distribution density of B orientation and the sum of distribution densities ofB orientation, S orientation and Cu orientation were determined.

(Tensile Test)

[0287] A test specimen was sampled from the copper alloy thin sheet and machined to produce a JIS No. 5 tensile test specimen such that the longitudinal direction of the test specimen runs in the direction orthogonal to the rolling direction of the sheet material. This test specimen was measured for mechanical properties including elongation under the conditions of room temperature, a test speed of 10.0 mm/min and GL = 50 mm by a universal tester Model 5882 manufactured by Instron Corp. Incidentally, the proof stress is tensile strength corresponding to a permanent elongation of 0.2%.

(Measurement of Electrical Conductivity)

[0288] A sample was extracted from the copper alloy thin sheet and measured for the electrical conductivity. In measuring the electrical conductivity of the copper alloy sheet sample, the sheet was worked into a strip-like test specimen of 10 mm (width) x 300 mm (length) by milling and measured for the electrical resistance by a double bridge-type resistance measuring apparatus according to the measuring method of electrical conductivity of nonferrous metal materials specified in JIS-HO505, and the electrical conductivity was calculated according to the average cross-sectional area method.

(Stress Relaxation Characteristic)

[0289] The copper alloy thin sheet was evaluated for the stress relaxation resistance characteristic in the orthogonal direction involving severer stress relaxation than in the parallel direction, with respect to the rolling direction by measuring the stress relaxation ratio in this direction. In the stress relaxation ratio measuring test below, a sample where the stress relaxation ratio in the direction orthogonal is less than 10% is judged as passed in terms of the stress relaxation resistance characteristic.

[0290] More specifically, in the measurement of the stress relaxation ratio, a test specimen was sampled from the copper alloy thin sheet and measured using the cantilever system shown in Fig. 3. A 10 mm-wide strip-like specimen 1 (with the length direction running in the direction orthogonal to the rolling direction of the sheet material) was cut out and fixed at one end to a rigid test board 2, and deflection in a size of d (= 10 mm) was given to the portion in a span length L of the specimen 1. At this time, L was determined such that a surface stress corresponding to 80% of the proof stress of the material was loaded on the material. After holding in an oven at 120°C for 3,000 hours, the specimen was taken out, and the permanent distortion δ after removing the deflection d was determined. The stress relaxation ratio (RS) was calculated according to the formula: $RS = (\delta/d) \times 100$.

(Evaluation Test of Bendability)

[0291] The bending test of the copper alloy sheet sample was performed according to Japan Copper and Brass Association Technical Standards. The sheet material was cut into a size of 10 mm (width) × 30 mm (length) and while applying bending in Bad Way (where bending axis is parallel to the rolling direction), the presence or absence of cracking in the bent part was observed through an optical microscope at a magnification of 50. At this time, the bending was performed under the conditions such that the ratio R/t of the minimum bend radius R to the sheet thickness t (0.25 mm) of the copper alloy sheet is as small as possible and becomes almost 0. The bendability was rated A when cracking was not observed, rated B when fine cracking was generated, and rated C when relatively large cracking was generated. Usually, a smaller R/t is rated as excellent bendability.

[0292] As apparent from Table 6, in Inventive Examples 44 to 55 using a copper alloy within the composition range of the third embodiment of the present invention in Table 5 (alloy Nos. 33 to 42), the copper alloy sheets are produced also within preferred conditions of the production method, such as cold rolling ratio (rolling reduction) per pass at the final cold rolling and the tension imposed on the copper alloy sheet when passing at the final annealing in a continuos heat-treating furnace. Accordingly, in Inventive Examples of Table 6, as the texture of the Cu-Ni-Sn-P-based copper alloy sheet, the distribution density of B orientation is 40% or less and at the same time, the sum of distribution densities of B orientation, S orientation and Cu orientation is from 30 to 90%.

[0293] In addition, it is presumed that in Inventive Examples, since the composition range is appropriate and the copper alloy sheet is produced within the above-described preferred conditions, production of a coarse Ni compound such as oxide, crystallized product or precipitate ofNi is suppressed and the amount of a fine Ni compound or the like or the amount ofNi contained as a solid solution can be ensured.

[0294] As a result, the copper alloy sheets of Inventive Examples 44 to 53 of Table 6 have, as terminal/connector properties, an electrical conductivity of 30% IACS or more and a stress relaxation ratio of less than 10% in the orthogonal direction involving severer stress relaxation, with respect to the rolling direction. In Inventive Examples, the bendability is excellent. Moreover, the copper alloy sheets of Inventive Examples further have, as mechanical properties, a 0.2%-proof stress of 500 MPa or more. That is, the copper alloy sheets of Inventive Examples are assured of high electrical conductivity and strength and excellent particularly in the stress relaxation resistance characteristic and bendability, revealing that the copper alloy sheet satisfies all of these properties at the same time.

[0295] However, out of Inventive Examples of Table 6, in Inventive Examples 54 and 55 (alloy Nos. 41 and 42 of Table 5) where the amount of other elements exceeds the preferred upper limit, the electrical conductivity is reduced as compared with other Inventive Examples where the electrical conductivity is relatively high. In Inventive Example 54, as shown in alloy No. 41 of Table 5, the total of elements in Element Group A: Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt is high to exceed the preferred upper limit of 1.0 mass%. In Inventive Example 55, as shown in alloy No. 42 of Table 5, the total of elements in Element Group B: Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal is high to exceed the preferred upper limit of 0.1 mass%.

[0296] In Inventive Example 48 of Table 6 (alloy No. 35 of Table 5), the Ni content is the lower limit of 0.1%; in Inventive Example 49 (alloy No. 36 of Table 5), the Ni content is the upper limit of 3.0%; in Inventive Example 50 (alloy No. 37 of Table 5), the Sn content is the lower limit of 0.01%; in Inventive Example 51 (alloy No. 38 of Table 5), the Sn content is the upper limit of 3.0%; in Inventive Example 52 (alloy No. 39 of Table 5), the P content is the lower limit of 0.01%; and in Inventive Example 53 (alloy No. 40 of Table 5), the P content is the upper limit of 0.3%.

[0297] Also, in Inventive Example 45 where the production conditions such as cold rolling ratio per pass at the final cold rolling and the tension imposed on the copper alloy sheet when passing at the final annealing in a continuous heat-treating furnace are on the lower limit side, the stress relaxation resistance characteristic and strength are relatively lower than those in Inventive Example 44.

[0298] In Comparative Examples 56 to 61 of Table 6, the copper alloy sheets are produced within preferred conditions of the production method such as rolling speed in final cold rolling and sheet passage rate in final annealing. Accordingly, in Comparative Examples 56 to 61, the Cu-Ni-Sn-P-based copper alloy sheet has the texture specified in the third embodiment of the present invention. Nevertheless, in these Comparative Examples, due to use of alloy Nos. 43 to 48 of Table 5 which are a copper alloy out of the composition range of the third embodiment of the present invention, any one of the electrical conductivity, strength, stress relaxation resistance characteristic and bendability is significantly inferior to Inventive Examples.

[0299] In Comparative Example 56 of Table 6, the Ni content deviates below the lower limit (alloy No. 43 of Table 5) and therefore, the strength and stress relaxation resistance characteristic are low. In Comparative Example 57, the Ni content deviates above the upper limit (alloy No. 44 of Table 5) and therefore, the balance between strength and electrical conductivity or the bendability is low.

[0300] In Comparative Example 58, the Sn content deviates below the lower limit (alloy No. 45 of Table 5) and therefore, the strength and stress relaxation resistance characteristic are excessively low. In the copper alloy of Comparative Example 59, the Sn content deviates above the upper limit (alloy No. 46 of Table 5) and therefore, the electrical conductivity and bendability are low.

[0301] In Comparative Example 60, the P content deviates below the lower limit (alloy No. 47 of Table 5) and therefore, the strength and stress relaxation resistance characteristic are low. In Comparative Example 61, the P content deviates above the upper limit (alloy No. 48 of Table 5) and therefore, cracking occurred during hot rolling, failing in characterization.

[0302] In Comparative Examples 62 and 63 of Table 6, a copper alloy within the composition range of the third embodiment of the present invention in Table 5 is used (alloy Nos. 33 and 34) and other production conditions are also within the preferred range, similarly to Inventive Examples. Nevertheless, the cold rolling ratio (rolling reduction) per pass at the final cold rolling or the tension imposed on the copper alloy sheet when passing at the final annealing in a continuous heat-treating furnace are out of the preferred range. In Comparative Example 62, the tension imposed on the sheet at the final annealing is substantially not present and is too small, and in Comparative Example 63, the cold rolling ratio per pass at the final cold rolling is too small and at the same time, the tension imposed on the sheet at the final annealing is too large.

[0303] As a result, in Comparative Examples 62 and 63, the texture of the Cu-Ni-Sn-P-based copper alloy sheet deviates from the texture specified in the third embodiment of the present invention. Accordingly, in these Comparative Examples, the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction is extremely inferior to Inventive Examples. Furthermore, the bendability is significantly poor as compared with Inventive Examples.

[0304] These results reinforce the meanings of the component composition and texture of the copper alloy in the third embodiment of the present invention for obtaining a Cu-Ni-Sn-P-based alloy sheet satisfying the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction and being excellent in the bendability and also in other properties required for a terminal or a connector, and further the meaning of the preferred production conditions for obtaining the texture.

Table 5

Class	No.	Chemical Component Composition of Copper Alloy Sheet (balance: Cu)									
		Ni	Sn	P	Fe	Zn	Mn	Si	Mg	Element Group A, #	Element Group B, #
Inventive Example	33	0.8	1.0	0.07	0.02	0.03	-	-	-	-	-
	34	1.0	0.9	0.06	0.02	-	-	0.01	0.01	-	-
	35	0.1	1.0	0.07	0.02	0.03	-	-	0.01	-	-
	36	3.0	1.0	0.07	0.02	0.03	-	-	-	-	-
	37	1.0	0.01	0.06	0.02	-	0.01	-	0.01	-	-
	38	0.6	3.0	0.04	0.02	-	0.01	-	-	-	-
	39	1.0	0.8	0.01	0.02	-	0.01	-	0.01	-	-
	40	1.0	0.8	0.3	0.02	-	0.01	-	-	-	-
	41	0.8	1.0	0.07	0.02	0.03	-	-	-	1.1	-
	42	0.8	1.0	0.07	0.02	0.03	-	-	-	-	0.2
Comparative Example	43	0.04	1.0	0.07	0.02	0.03	-	-	-	-	-
	44	3.2	1.0	0.07	0.02	0.03	0.01	-	-	-	-
	45	0.8	-	0.07	0.02	0.03	-	0.01	-	-	-
	46	0.8	3.2	0.07	0.02	0.03	-	-	0.01	-	-
	47	0.8	1.0	0.004	0.02	0.03	-	-	0.01	-	-
	48	0.8	1.0	0.35	0.02	0.03	0.01	-	-	-	-

* "-" indicates that the content is below the detection limit.

* Other Element Group A: the total content of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt.

* Other Element Group B: the total content of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal.

Table 6

Class	No.	Alloy No. of Table 5	Final Cold Rolling, Cold Rolling Ratio (%)	Final Continuous Annealing, Sheet Passage Tension (kgf/mm^2)	Texture of Copper Alloy Sheet		Properties of Copper Alloy Sheet				
					B Orientation Density (%)	B+S+CU Orientation Density (%)	Electrical Conductivity (%IACS)	Tensile Strength (MPa)	0.2%-Proof Stress (MPa)	Stress Relaxation Ratio (%)	Bendability (R/t)
Inventive Example	44	33	30	4	29	67	36	565	540	7	A
	45	33	10	0.5	14	33	37	535	520	9	A
	46	33	50	3	32	74	35	570	550	8	A
	47	34	20	4	24	56	38	535	520	8	A
	48	35	40	3	28	63	40	530	510	9	A
	49	36	30	2	20	45	34	570	555	7	A
	50	37	30	7	37	84	45	520	500	8	A
	51	38	20	2	18	41	30	625	605	8	A
	52	39	40	2	23	51	43	515	500	9	A
	53	40	30	1	17	37	32	600	580	9	A
	54	41	30	5	31	71	28	650	635	7	A
	55	42	30	5	30	69	29	640	620	7	A
Comparative Example	56	43	40	2	35	77	40	505	490	11	A
	57	44	30	3	40	85	33	550	530	7	C
	58	45	10	5	29	62	46	485	465	9	A
	59	46	30	1	15	31	27	635	615	8	C
	60	47	20	2	23	50	43	495	480	11	A
	61	48	-	-	-	-	-	-	-	-	-
	62	33	10	none	10	24	37	530	515	11	B
	63	34	5	10	44	95	38	540	520	12	C

(4) Fourth Example (Example According to Fourth Embodiment of the Present Invention)

[0305] Working examples according to the fourth embodiment of the present invention are described below. Copper alloy thin sheets varied in the half-value breadth (dislocation density) of the X-ray diffraction intensity peak from {200} plane in the sheet surface were produced by changing the roll diameter and minimum rolling reduction per pass in the final cold rolling. These copper alloy thin sheets each was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress, shear plane ratio and stress relaxation resistance characteristic.

[0306] More specifically, a copper alloy having a chemical component composition shown in Table 7 (the balance of the composition excluding the element amounts shown is Cu) was melted in a coreless furnace and then subjected to ingot making by a semicontinuous casting method (cold solidification rate of casting: 2°C/sec) to obtain an ingot of 70 mm (thickness) × 200 mm (width) × 500 mm (length). The obtained ingots were rolled in common under the following conditions to obtain a copper alloy thin sheet. After the surface of each ingot was scalped and heated, the ingot was heated at 960°C in a heating furnace and immediately hot-rolled at a hot rolling finishing temperature of 750°C into a 16 mm-thick sheet, and the sheet was quenched in water from a temperature of 650°C or more.

[0307] In this process, the time required from the completion of addition of alloy elements to the initiation of casting in the melting furnace was set to 1,200 seconds or less commonly among respective Examples, and the time required from the extraction out of the heating furnace to the completion of hot rolling was set to 1,200 seconds or less commonly among respective Examples.

[0308] After the removal of oxide scales, the sheet was subjected to cold rolling, continuous finish annealing, cold rolling and strain relief annealing in this order to produce a copper alloy thin sheet. That is, the sheet after primary cold rolling (rough cold rolling, intermediate cold rolling) was scalped. Finish annealing of the sheet was performed in an annealing furnace at the maximum peak temperature of 600°C in terms of the substantial temperature of the sheet by holding the sheet at this temperature for 60 seconds.

[0309] After the finish annealing, final cold rolling at a rolling reduction of 60% was performed. The roll diameter (mm) and minimum rolling reduction (%) per pass in this final cold rolling are shown in Table 7. Incidentally, a roll having the same roll diameter was used in all of 4 passes of the final cold rolling. Also, even though the roll diameter was changed, the roll length was set constant at 500 mm in common. After the final cold rolling, low-temperature strain relief annealing was performed under the conditions of substantial temperature of 400°C × 20 seconds to obtain a copper alloy thin sheet having a thickness of 0.25 mm.

[0310] In all of the copper alloys shown in Table 7, the balance of the composition excluding the element amounts shown is Cu, and the content of elements of Group A, that is, Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, as other impurity elements was 1.0 mass% or less in total of these elements, except for Inventive Example 57 of Table 7 (Inventive Example 73 of Table 8).

[0311] Also, the content of elements of Group B, that is, Hf, Th, Li, Na, K, Sr, Pd, W, S, Si, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, was 0.1 mass% or less in total of these elements, except for Inventive Example 58 of Table 7 (Inventive Example 74 of Table 8).

[0312] In each of Examples, a sample was cut out from the obtained copper alloy sheet, and the sample was evaluated for various properties such as electrical conductivity, tensile strength, 0.2%-proof stress, shear plane ratio and stress relaxation resistance characteristic. The results obtained are shown in Table 8.

(Measurement of Half-Value Breadth)

[0313] An X-ray diffraction pattern of the copper alloy sheet sample was obtained by a normal X-ray diffraction method under the conditions of a tube voltage of 40 kV, a tube current of 200 mA, a scan rate of 2°/min, a sampling width of 0.02° and a measurement range (2θ) of 30 to 115° by using an X-ray diffraction analyzer (Model: RINT 1500) manufactured by Rigaku Corporation and using Co as the target. From this pattern, the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface was determined by the method described above. The measurement was performed at two portions and an average of the values obtained was used as the half-value breadth.

(Tensile Test)

[0314] A test specimen was sampled from the copper alloy thin sheet and machined to produce a JIS No. 5 tensile test specimen such that the longitudinal direction of the test specimen runs in the direction orthogonal to the rolling direction of the sheet material. This test specimen was measured for mechanical properties including elongation under the conditions of room temperature, a test speed of 10.0 mm/min and GL = 50 mm by a universal tester Model 5882 manufactured by Instron Corp. Incidentally, the proof stress is tensile strength corresponding to a permanent elongation of 0.2%.

(Measurement of Electrical Conductivity)

[0315] A sample was extracted from the copper alloy thin sheet and measured for the electrical conductivity. In measuring the electrical conductivity of the copper alloy sheet sample, the sheet was worked into a strip-like test specimen of 10 mm (width) × 300 mm (length) by milling and measured for the electrical resistance by a double bridge-type resistance measuring apparatus according to the measuring method of electrical conductivity of nonferrous metal materials specified in JIS-H0505, and the electrical conductivity was calculated according to the average cross-sectional area method.

(Measurement of Burr Height)

[0316] The burr height of the copper alloy sheet sample was measured under the above-described test conditions. The sample was rated A when the burr height was 5 μm or less, rated B when the burr height was from 5 to 10 μm, and rated C when the burr height exceeded 10 μm.

(Stress Relaxation Characteristic)

[0317] The copper alloy thin sheet was evaluated for the stress relaxation resistance characteristic in the orthogonal direction involving severer stress relaxation than in the parallel direction, with respect to the rolling direction by measuring the stress relaxation ratio in this direction. In the stress relaxation ratio measuring test below, a sample where the stress relaxation ratio in the direction orthogonal to the rolling direction is less than 10% is judged as passed in terms of the stress relaxation resistance characteristic.

[0318] More specifically, in the measurement of the stress relaxation ratio, a test specimen was sampled from the copper alloy thin sheet and measured using the cantilever system shown in Fig. 3. A 10 mm-wide strip-like specimen 1 (with the length direction running in the direction orthogonal to the rolling direction of the sheet material) was cut out and fixed at one end to a rigid test board 2, and deflection in a size of d (= 10 mm) was given to the portion in a span length L of the specimen 1. At this time, L was determined such that a surface stress corresponding to 80% of the proof stress of the material was loaded on the material. After holding in an oven at 120°C for 3,000 hours, the specimen was taken out, and the permanent distortion δ after removing the deflection d was determined. The stress relaxation ratio (RS) was calculated according to the formula: $RS = (\delta/d) \times 100$.

[0319] As apparent from Table 8, in Inventive Examples 64 to 74 using a copper alloy within the composition range of the fourth embodiment of the present invention in Table 7 (alloy Nos. 49 to 58), the copper alloy sheets are produced within preferred conditions of the production method such as roll diameter and minimum rolling reduction per pass in final cold rolling. Accordingly, in Inventive Examples of Table 8, the copper alloy sheet has a dislocation density such that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface by the peak height is 1.0×10^{-4} or more.

[0320] In addition, it is presumed that in Inventive Examples, since the composition range is appropriate and the copper alloy sheet is within the above-described preferred conditions, production of a coarse Ni compound such as oxide, crystallized product or precipitate ofNi is suppressed and the amount of a fine Ni compound or the like or the amount ofNi contained as a solid solution can be ensured.

[0321] As a result, the copper alloy sheets of Inventive Examples 64 to 72 have, as terminal/connector properties, an electrical conductivity of 30% IACS or more and a stress relaxation ratio of less than 10% in the orthogonal direction involving severer stress relaxation, with respect to the rolling direction and further have, as mechanical properties, a 0.2%-proof stress of 500 MPa or more and excellent press punchability. That is, the copper alloy sheets of Inventive Examples are assured of high electrical conductivity and strength and excellent particularly in the press punchability and stress relaxation resistance characteristic, revealing that the copper alloy sheet satisfies all of these properties at the same time.

[0322] However, out of Inventive Examples of Table 8, in Inventive Examples 73 and 74 (alloy Nos. 57 and 58 of Table 7) where the amount of other elements exceeds the preferred upper limit, the electrical conductivity is reduced as compared with other Inventive Examples where the electrical conductivity is relatively high. In Inventive Example 73, as shown in alloy No. 57 of Table 7, the total of elements in Element Group A: Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt is high to exceed the preferred upper limit of 1.0 mass%. In Inventive Example 74, as shown in alloy No. 58 of Table 7, the total of elements in Element Group B: Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal is high to exceed the preferred upper limit of 0.1 mass%.

[0323] In Inventive Example 67 of Table 8 (alloy No. 51 of Table 7), the Ni content is the lower limit of 0.1%; in Inventive Example 68 (alloy No. 52 of Table 7), the Ni content is the upper limit of 3.0%; in Inventive Example 69 (alloy No. 53 of Table 7), the Sn content is the lower limit of 0.01%; in Inventive Example 70 (alloy No. 54 of Table 7), the Sn content is the upper limit of 3.0%; in Inventive Example 71 (alloy No. 55 of Table 7), the P content is the lower limit of 0.01%; and in Inventive Example 72 (alloy No. 56 of Table 7), the P content is the upper limit of 0.3%.

[0324] Also, in Inventive Example 65 where the production conditions such as roll diameter and minimum rolling reduction per pass in final cold rolling are on the lower limit side, the stress relaxation resistance characteristic and strength are relative lower than in Inventive Example 64.

[0325] In Comparative Examples 75 to 80 of Table 8, the copper alloy sheets are produced within preferred conditions of the production method such as roll diameter and minimum rolling reduction per pass in final cold rolling. Accordingly, in Comparative Examples 75 to 80, the copper alloy sheet has a dislocation density such that the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface by the peak height is 1.0×10^{-4} or more. Nevertheless, in these Comparative Examples, due to use of alloy Nos. 59 to 64 of Table 7 which are a copper alloy out of the composition range of the fourth embodiment of the present invention, any one of the electrical conductivity, strength, stress relaxation resistance characteristic and press punchability is significantly inferior to Inventive Examples.

[0326] In Comparative Example 75 of Table 8, the Ni content deviates below the lower limit (alloy No. 59 of Table 7), as a result, the strength and stress relaxation resistance characteristic are low and the press punchability is also poor due to low strength. In Comparative Example 76, the Ni content deviates above the upper limit (alloy No. 60 of Table 7) and therefore, the balance between strength and electrical conductivity is low.

[0327] In Comparative Example 77, the Sn content deviates below the lower limit (alloy No. 61 of Table 7), as a result, the strength is too low and the press punchability is also poor. In the copper alloy of Comparative Example 78, the Sn content deviates above the upper limit (alloy No. 62 of Table 7) and therefore, the electrical conductivity is low.

[0328] In Comparative Example 79, the P content deviates below the lower limit (alloy No. 63 of Table 7) and therefore, the strength, stress relaxation resistance characteristic and press punchability are low. In Comparative Example 80, the P content deviates above the upper limit (alloy No. 64 of Table 7) and therefore, cracking occurred during hot rolling, failing in characterization.

[0329] In Comparative Examples 81 and 82 of Table 8, a copper alloy within the composition range of the fourth embodiment of the present invention in Table 7 is used (alloy Nos. 49 and 50) and other production conditions are also within the preferred range, similarly to Inventive Examples. Nevertheless, only the conditions of the final cold rolling are out of the preferred range. In Comparative Example 81, the minimum rolling reduction (%) per pass of the final cold rolling is too small, and in Comparative Example 82, the roll diameter (mm) of the final cold rolling is too large and the minimum rolling reduction (%) per pass is too small.

[0330] As a result, in Comparative Examples 81 and 82, the value obtained by dividing the half-value breadth of the X-ray diffraction intensity peak from {200} plane in the sheet surface by the peak height is less than 1.0×10^{-4} and the dislocation density is too small. In turn, in these Comparative Examples, the press punchability is significantly poor as compared with Inventive Examples. Furthermore, the strength and stress relaxation resistance characteristic are also lower than in Inventive Examples.

[0331] These results reinforce the meanings of the component composition and texture of the copper alloy in the fourth embodiment of the present invention for obtaining a Cu-Ni-Sn-P-based alloy sheet satisfying the press punchability and being excellent in other properties required for a terminal or a connector, such as strength and stress relaxation resistance characteristic, and further the meaning of the preferred production conditions for obtaining the texture.

Table 7

Class	No.	Chemical Component Composition of Copper Alloy Sheet (balance: Cu)									
		Ni	Sn	P	Fe	Zn,	Mn	Si	Mg	Element Group A	Element Group B
Inventive Example	49	0.7	1.2	0.05	0.02	0.05	-	-	-	-	-
	50	1.2	0.7	0.07	0.02	-	-	0.01	-	-	-
	51	0.1	1.2	0.05	0.02	0.05	-	-		-	-
	52	3.0	1.2	0.05	0.02	-	0.01	-	-	-	-
	53	0.7	0.01	0.05	0.02	0.05	-	-	0.01	-	-
	54	0.5	3.0	0.04	0.02	-	-	0.01	-	-	-
	55	1.2	0.7	0.01	0.02	-	-	-	0.01	-	-
	56	1.2	0.7	0.3	0.02	-	0.01	-	-	-	-
	57	0.7	1.2	0.05	0.02	0.05	0.01	-	-	1.3	-
	58	0.7	1.2	0.05	0.02	0.05	-	-	-	-	0.2

(continued)

Class	No.	Chemical Component Composition of Copper Alloy Sheet (balance: Cu)									
		Ni	Sn	P	Fe	Zn,	Mn	Si	Mg	Element Group A	Element Group B
Comparative Example	59	0.04	1.2	0.05	0.02	0.05	0.01	-	-	-	-
	60	3.2	1.0	0.05	0.02	-	-	0.01	-	-	-
	61	0.7	-	0.05	0.02	0.05	-	-	-	-	-
	62	0.7	3.2	0.05	0.02	-	0.01	-	0.01	-	-
	63	0.7	1.2	0.004	0.02	0.05	-	-	-	-	-
	64	0.7	1.2	0.35	0.02	-	-	-	0.01	-	-

* "-" indicates that the content is below the detection limit.
* Other Element Group A: the total content of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt.
* Other Element Group B: the total content of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal.

Table 8

Class	No.	Alloy No. of Table 7	Final Cold Rolling		Texture of Copper Alloy Sheet	Properties of Copper Alloy Sheet				
			Roll Diameter (mm)	Minimum Rolling Reduction (%/1 pass)	Half-Value Breadth of X-Ray Diffraction (200) Plane Intensity Peak/Peak Height ($\times 10^{-4}$)	Electrical Conductivity (%IACS)	Tensile Strength (MPa)	0.2%-Proof Stress (MPa)	Stress Relaxation Ratio (%)	Press Punchability
Inventive Example	64	49	60	30	1.6	35	595	575	7	A
	65	49	70	20	1.2	36	570	555	9	A
	66	50	60	20	1.2	37	565	545	8	A
	67	51	70	20	1.1	40	540	525	9	A
	68	52	60	20	1.5	34	585	570	7	A
	69	53	60	20	1.1	44	520	505	9	A
	70	54	50	40	2.0	30	640	620	7	A
	71	55	60	20	1.2	43	520	505	9	A
	72	56	50	40	1.6	32	620	600	8	A
	73	57	60 50	40	1.8	27	650	635	7	A
	74	58		30	1.7	29	635	620	9	A
Comparative Example	75	59	60	20	1.1	39	505	485	11	B
	76	60	50	20	1.4	30	570	555	7	A
	77	61	60	20	1.2	43	490	470	9	B
	78	62	60	30	1.7	25	640	620	7	A
	79	63	60	20	1.0	41	500	480	11	B
	80	64	-	-	-	-	-	-	-	-
	81	49	60	10	0.90	36	545	530	11	C
	82	50	100	10	0.71	38	530	515	12	C

[0332] While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope thereof.

[0333] This application is based on Japanese Patent Application No. 2007-205630 filed August 7, 2007, Japanese Patent Application No. 2007-232641 filed September 7, 2007, Japanese Patent Application No. 2007-252036 filed September 27, 2007, and Japanese Patent Application No. 2007-252037 filed September 27, 2007, the entire contents thereof being hereby incorporated by reference.

[0334] Furthermore, all references cited herein are incorporated in their entireties.

INDUSTRIAL APPLICABILITY

[0335] As described in the foregoing pages, according to the first embodiment of the present invention, a Cu-Ni-Sn-P-based alloy sheet with excellent strength-ductility balance, which is responsive to the high-efficiency high-speed press forming process for producing a connection component such as automotive terminal or connector and satisfies also the properties required for a terminal or connector, can be provided.

[0336] According to the second embodiment of the present invention, a Cu-Ni-Sn-P-based alloy sheet satisfying the stress relaxation resistance characteristic in the direction orthogonal to the rolling direction, creating not so much difference from the stress relaxation resistance characteristic in the direction parallel to the rolling direction, and being excellent also in other properties required for a terminal or a connector, can be provided.

[0337] According to the third embodiment of the present invention, a Cu-Ni-Sn-P-based alloy sheet satisfying the stress relaxation resistance characteristic in the direction orthogonal to rolling and being excellent in bendability and also in other properties required for a terminal or a connector, can be provided.

[0338] According to the fourth embodiment of the present invention, a Cu-Ni-Sn-P-based alloy sheet satisfying the press punchability and being excellent also in other properties required for a terminal or a connector, such as strength and stress relaxation resistance characteristic, can be provided.

[0339] Accordingly, the present invention is suitable particularly for a connection component such as automotive terminal or connector.

Claims

1. A copper alloy sheet comprising, in terms of mass%, 0.1 to 3.0% of Ni, 0.01 to 3.0% of Sn and 0.01 to 0.3% ofP, with the balance being copper and inevitable impurities, wherein the copper alloy sheet has a ratio I(200)/I(220) of a X-ray diffraction intensity I(200) from (200) plane in the sheet surface to a X-ray diffraction intensity I(220) from (220) plane in the sheet surface of 0.25 or less, and has an average grain size of 5.0 μm or less.

2. The copper alloy sheet as claimed in claim 1, which further comprises at least one member selected from the group consisting of, in terms of mass%, 0.5% or less of Fe, 1% or less of Zn, 0.1% or less of Mn, 0.1% or less of Si and 0.3% or less of Mg.

3. The copper alloy sheet as claimed in claim 1 or 2, which further comprises at least one member selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt, in a total amount of 1.0 mass% or less.

4. The copper alloy sheet as claimed in any one of claims 1 to 3, which further comprises at least one member selected from the group consisting of Hf, Th, Li, Na, K, Sr, Pd, W, S, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B and Misch metal, in a total amount of 0.1 mass% or less.

Fig. 1

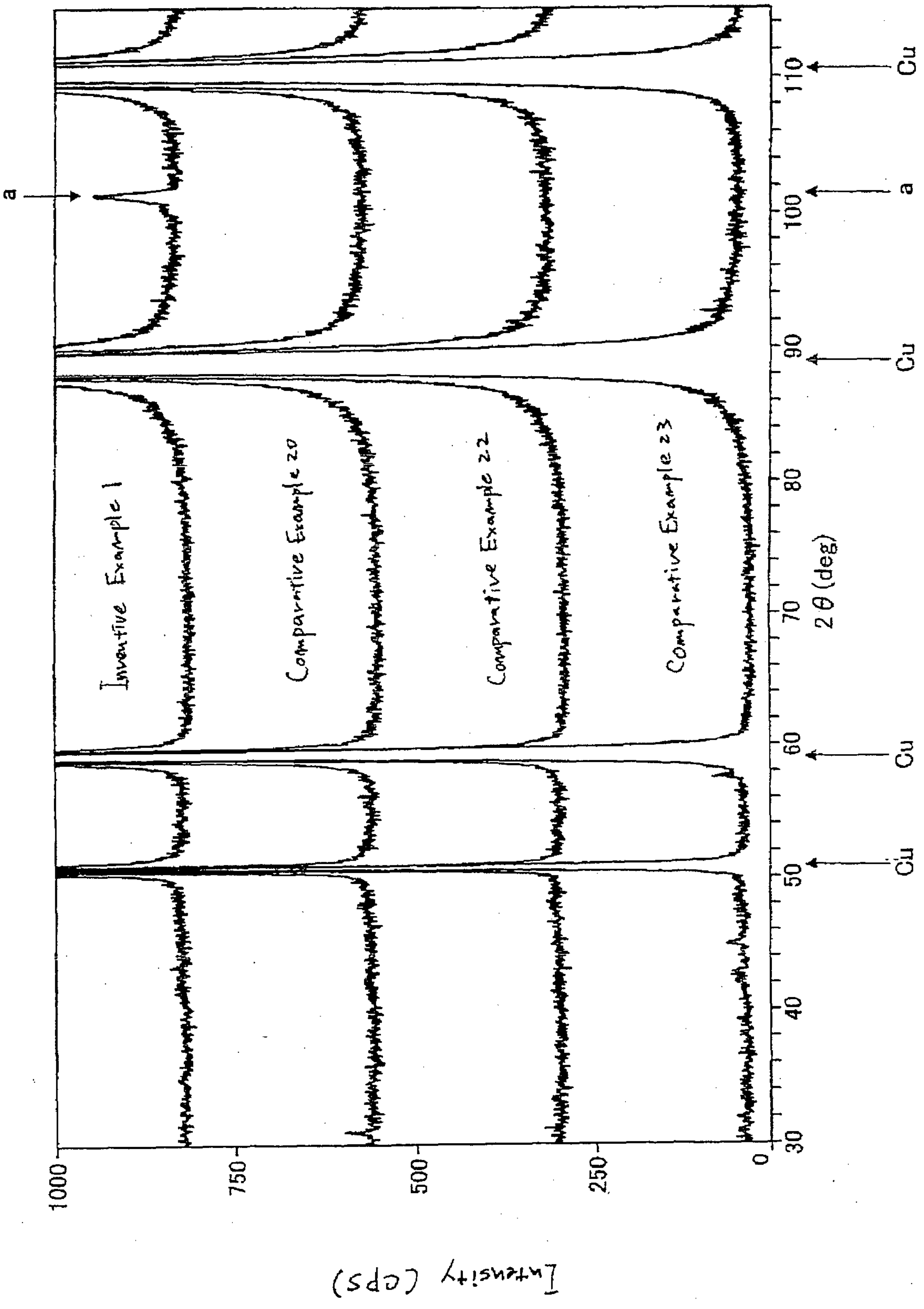

a
Inventive Example 1
Comparative Example 20
Comparative Example 22
Comparative Example 23
Cu
Cu
Cu
a
Cu
30
40
50
60
70
80
90
100
110
2θ (deg)
0
250
500
750
1000
Intensity (cps)

Fig. 2

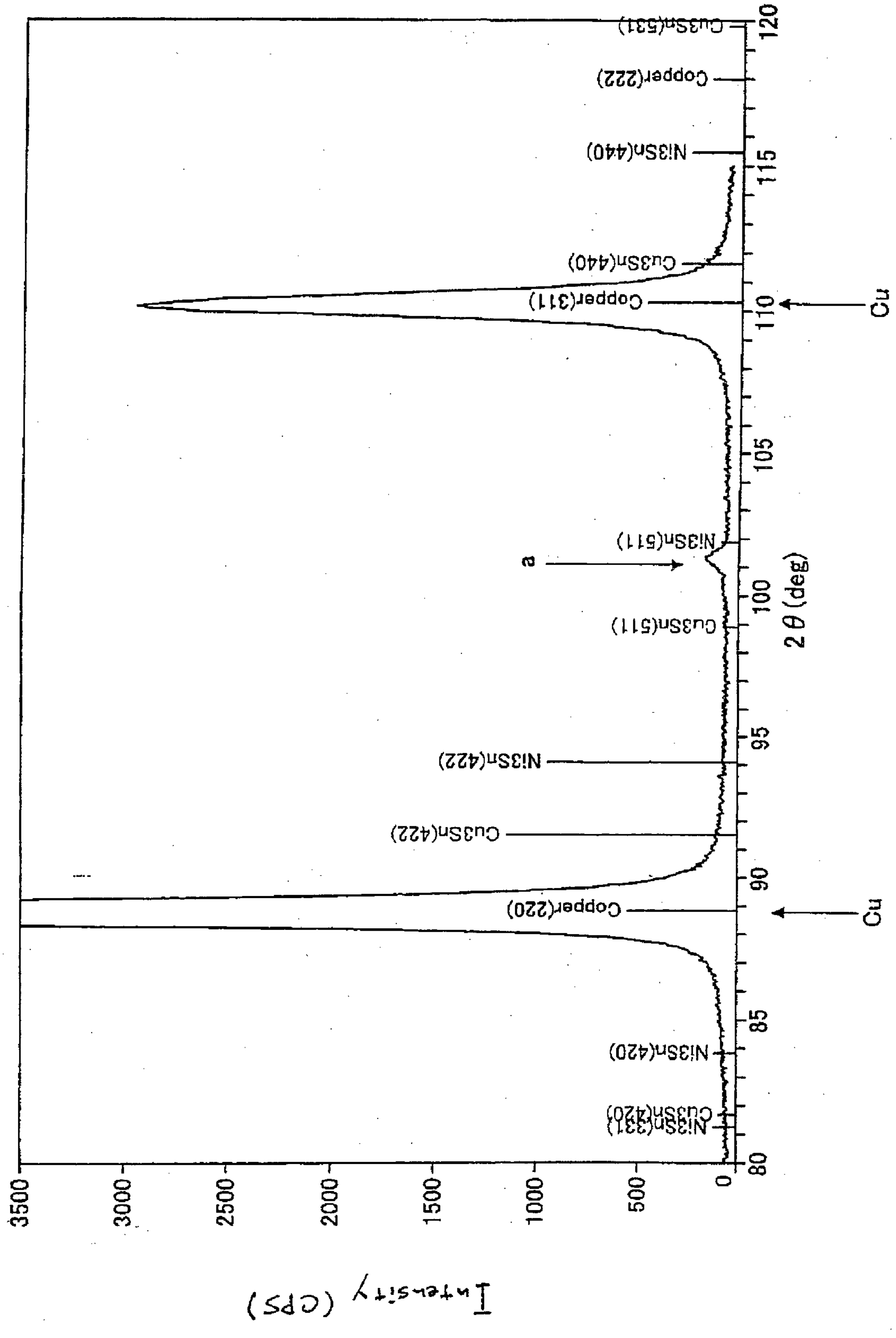

Cu3Sn(531)
Copper(222)
Ni3Sn(440)
Cu3Sn(440)
Copper(311)
Cu
Ni3Sn(511)
a
Cu3Sn(511)
Ni3Sn(422)
Cu3Sn(422)
Copper(220)
Cu
Ni3Sn(420)
Cu3Sn(420)
Ni3Sn(331)
80
85
90
95
100
105
110
115
120
2θ (deg)
0
500
1000
1500
2000
2500
3000
3500
Intensity (CPS)

Fig. 3

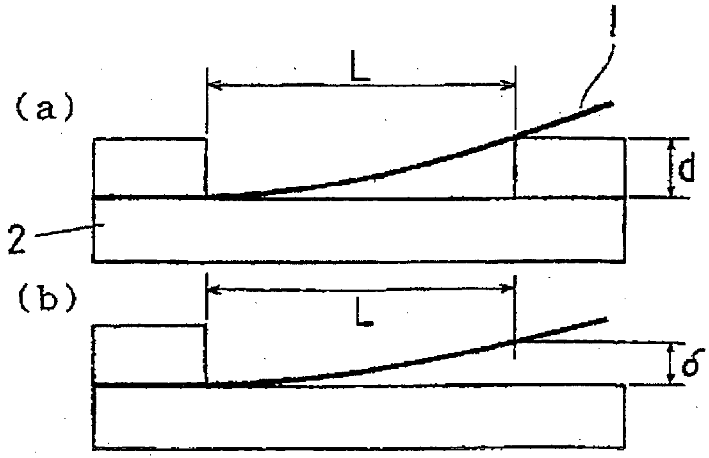


Fig. 4

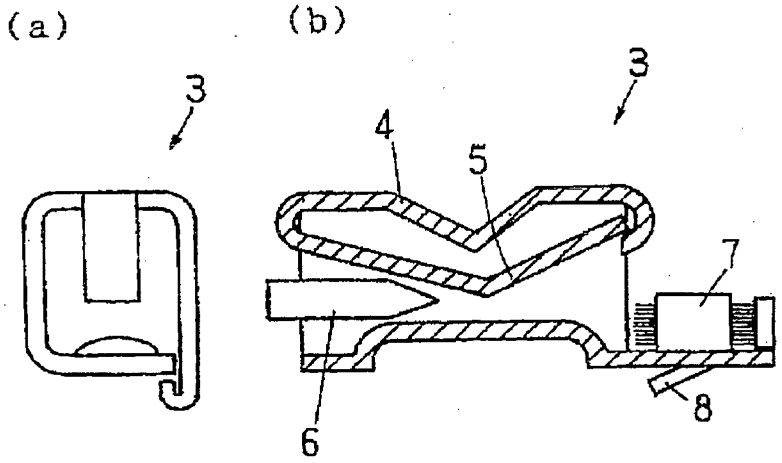


Fig. 5

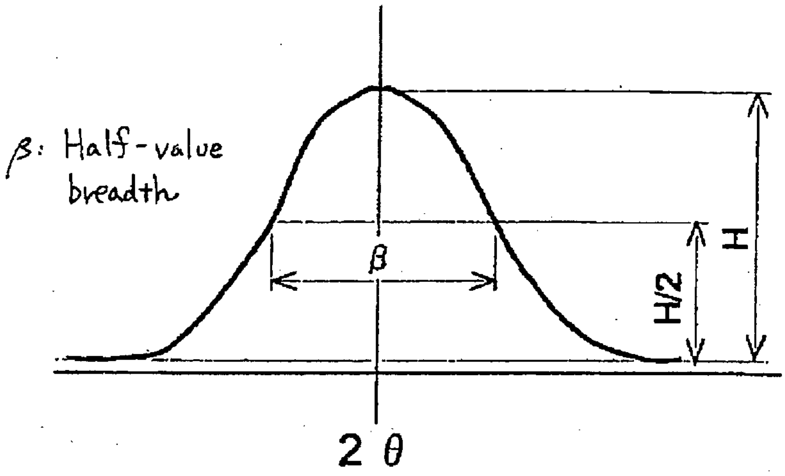
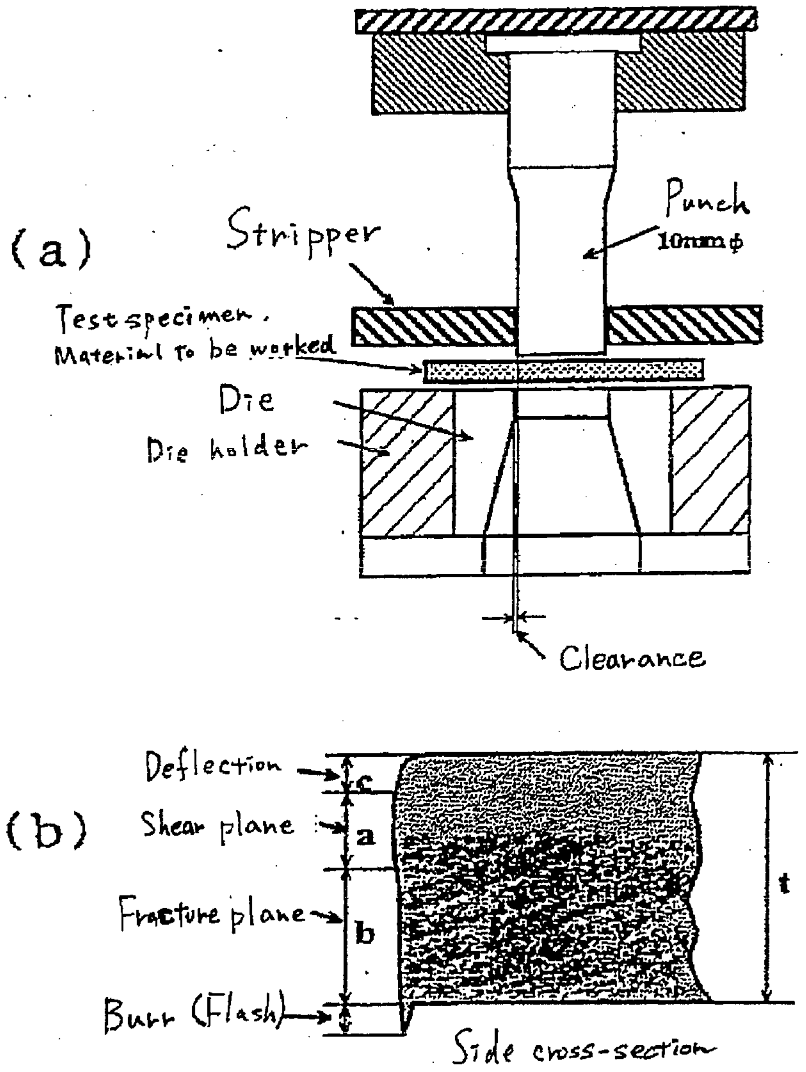


Fig. 6


(a)
Stripper
Punch
10mmϕ
Test specimen,
Material to be worked
Die
Die holder
Clearance
(b)
Deflection
c
Shear plane
a
Fracture plane
b
Burr (Flash)
t
Side cross-section

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