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(54) **COPPER ALLOY, COPPER ALLOY PLATE, AND PROCESS FOR PRODUCING THE SAME**

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(57) **ABSTRACT**

A copper alloy with an excellent stress relaxation resistance including Ni: 0.1 through 3.0 mass %, Sn: 0.01 through 3.0 mass %, P: 0.01 through 0.3 mass % and remainder copper and inevitable impurities, and the Ni content in extracted residues separated and left on a filter having filter mesh size of 0.1 μm by using an extracted residues method accounting for 40 mass % or less of the Ni content in the copper alloy, wherein the extracted residues method requires that 10 g of the copper alloy is immersed in 300 ml of a methanol solution which contains 10 mass % of ammonium acetate, and using the copper alloy as the anode and platinum as the cathode, constant-current electrolysis is performed at the current density of 10 mA/cm$^2$, and the solution in which the copper alloy is thus dissolved is subjected to suction filtration using a membrane filter of polycarbonate whose filter mesh size is 0.1 μm, thereby separating and extracting undissolved residues on said filter, and the Ni content in the extracted residues is identified through analysis by ICP after dissolving said undissolved residues separated and left on said filter into a solution prepared by mixing aqua regia and water at the ratio of 1:1.

Fig 1

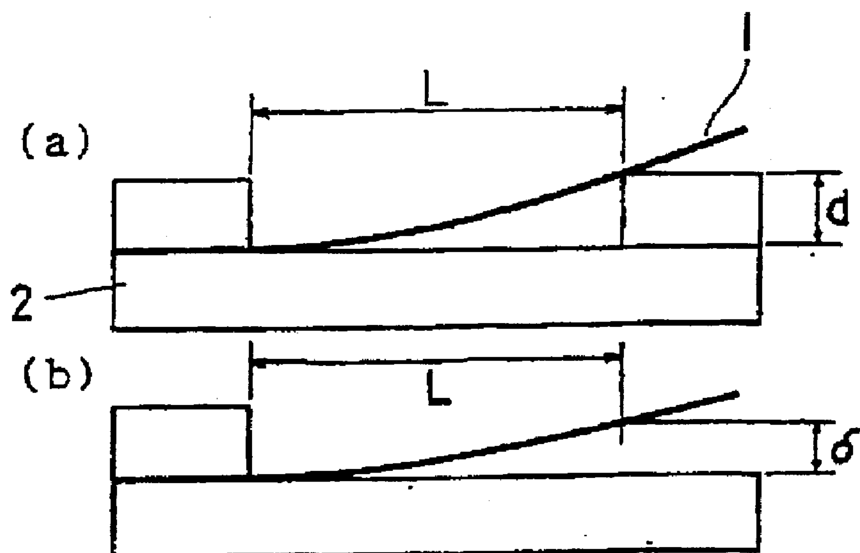
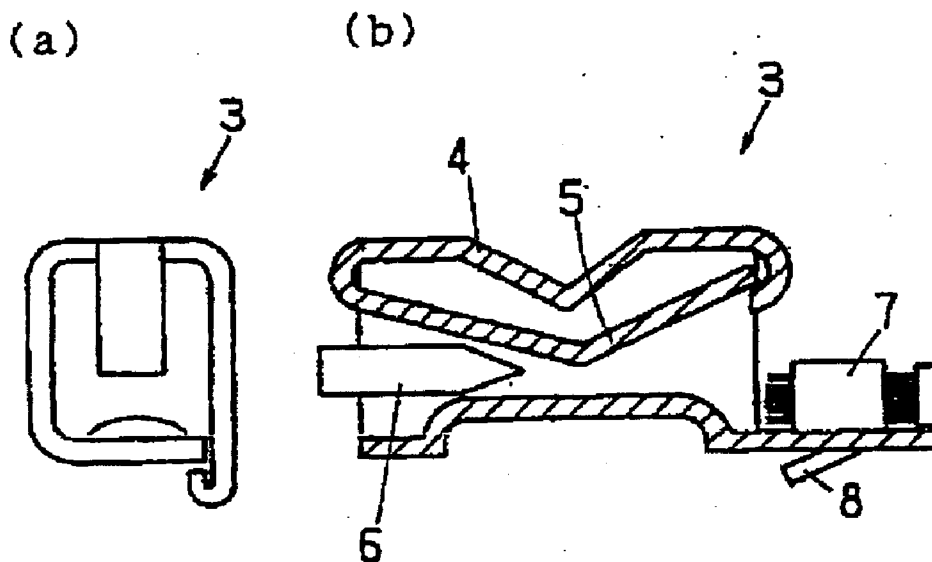



Fig 2



# COPPER ALLOY, COPPER ALLOY PLATE, AND PROCESS FOR PRODUCING THE SAME

## BACKGROUND OF THE INVENTION

**[0001]** 1. Field of the Invention

**[0002]** The present invention relates to a copper alloy and a copper alloy plate which are excellent in bending formability, shear stamping workability and stress relaxation resistance and which are suitable for use particularly as an automotive terminal, an automotive connector and the like, and also to a method for manufacturing such a copper alloy and such a copper alloy plate.

**[0003]** 2. Description of the Related Art

**[0004]** Connection parts such as automotive terminals and automotive connectors are demanded to be manufactured at low costs but yet remain reliable in their capabilities even in a high-temperature environment as that inside an engine room these days. One of the most important properties to secure the demanded reliability even in a high-temperature environment is a capability of maintaining locking at a contact point, which is usually called a "stress relaxation resistance". In other words, where a tab of a male terminal is locked in a spring-shaped contact point of a female terminal for instance, these connection components held in a high-temperature environment as that inside an engine room start losing their capabilities of remaining locked in the contact point upon application of steady displacement upon a spring-shaped component made of a copper alloy, and a stress relaxation resistance is a resistive characteristic against this.

**[0005]** Copper alloys superior in stress relaxation resistance are a Cu—Ni—Si alloy, a Cu—Ti alloy, a Cu—Be alloy and the like, as already known. Containing strongly oxidizing elements (such as Si, Ti and Be), these alloys will not melt inside a large-scale melting furnace which opens wide to the atmosphere and are therefore inevitably expensive to make.

**[0006]** In contrast, an alloy primarily made of Cu—Ni—Sn—P containing a relatively small amount of additive elements can be made as an ingot inside a shaft furnace at a high productivity and therefore demands only an extremely low cost. As for a Cu—Ni—Sn—P alloy as well, various proposals have been made in an effort to improve its stress relaxation resistance. This is a very promising alloy system which could be capable of exhibiting a stress relaxation resistance equivalent to that of a Cu—Be alloy depending upon a manufacturing method and the amount of additive elements.

**[0007]** For example, Patent Document 1 (JPB 2844120) discloses a method of making a copper-based alloy for use as a connector which exhibits an excellent stress relaxation resistance. According to this manufacturing method, Ni—P intermetallic compounds are dispersed finely and uniformly in the matrix of a Cu—Ni—Sn—P alloy to thereby enhance the electric conductivity while at the same time improving the stress relaxation resistance and other properties, and this patent document describes that it is necessary to strictly control the start of cooling during hot rolling, the temperature at the end point of hot rolling, the cooling temperature during hot rolling and also the temperature and the duration of a 5-720 minute heat treatment which is carried out in the middle of cold rolling which follows hot rolling, in order to obtain desired characteristics.

**[0008]** Meanwhile, Patent Documents 2 (JPA 11-293367) and 3 (JPA 2002-294368) disclose, in relation to a Cu—Ni—Sn—P alloy exhibiting an excellent stress relaxation resistance and a method of making the same, lowering the P content as much as possible and accordingly suppressing precipitation of Ni—P compounds to thereby make a solid solution copper alloy. Not needing a sophisticated heat treatment technique, this method promises an advantage that it is possible to make the alloy by an anneal heat treatment in an extremely short period of time.

## SUMMARY OF THE INVENTION

**[0009]** JASO-C400, the standard set by The Society of Automotive Engineers of Japan, requires with respect to the stress relaxation resistance that the stress relaxation ratio after holding at 150 degrees Celsius for 1,000 hours is 15% or lower. FIG. **1**, in the sections (a) and (b), show a stress relaxation resistance testing machine. Using this testing machine, a test specimen **1** cut out in a rectangular shape is fixed at its one end to a rigid body test bench **2** and then cantilevered at the other end and consequently bent (the amount of bending is d), and after maintaining this state at a predetermined temperature for a predetermined period of time, unloading is done at a room temperature and the amount of post-loading bending (permanent strain) δ is calculated. The stress relaxation ratio (RS) is expressed as:

$$RS=(\delta/d)\times 100$$

**[0010]** The stress relaxation ratio of a copper alloy plate is anisotropic and has a different value depending upon how the longitudinal direction of a test specimen extends relative to the rolling direction of the copper alloy plate. In general, the stress relaxation ratio is lower when the longitudinal direction is parallel to the rolling direction than when the longitudinal direction is perpendicular to the rolling direction. However, The JASO standard mentioned above does not specify this direction, which has led to an understanding that the stress relaxation ratio needs be 15% or less in any one of the parallel direction and the perpendicular direction to the rolling direction. The recent years nevertheless have seen people believing that a high stress relaxation resistance in the perpendicular direction to the rolling direction of a copper alloy plate is desirable.

**[0011]** FIG. **2** shows a cross sectional structure of a typical box-shaped connector (female terminal **3**). In FIG. **2**, an upper holder section **4** supports a push part **5** in a cantilever posture, and insertion of a male terminal **6** elastically deforms the push part **5**, whereby the reaction force to the deformation fixes the male terminal **6**. Denoted at **7** is a wire connecting part and denoted at **8** is a fixing segment in FIG. **2**. During manufacturing of the female terminal **3** by means of press working of a copper alloy plate, in the blank layout for the female terminal **3**, the longitudinal direction of the female terminal **3** (i.e., the longitudinal direction of the push part **5**) is directed perpendicular to the rolling direction. The push part **5** is demanded to exhibit a particularly high stress relaxation resistance against bending (elastic deformation) of the push part **5** along the longitudinal direction of the push part **5**. Hence, the copper alloy plate must exhibit a particularly high stress relaxation resistance along the perpendicular direction to its rolling direction.

**[0012]** In contrast, the solid solution copper alloys described in Patent Documents 2 and 3 mentioned above almost have a high stress relaxation resistance which manifests itself as a stress relaxation ratio of 15% or lower in the parallel direction to the rolling direction, although not achieving the same in the perpendicular direction to the rolling direction.

**[0013]** Noting this, as for this type of a solid solution copper alloy, users are asking for a high stress relaxation resistance which manifests itself as a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction rather than along the parallel direction to the rolling direction.

**[0014]** Further, the chemical energy needed for making Ni—P intermetallic compounds is extremely low, which has led to a problem that Ni—P intermetallic compounds size easily become coarse by a heat treatment during copper alloy production and bending formability of the copper alloy, which is evidence of an accurate terminal shape, deteriorates although its stress relaxation resistance is high enough to meet the requirement set by the present automotive technologies and that stamping-induced flashes are large which will wear away metal dies for press working of terminals.

**[0015]** Referring to the cross sectional structure of the typical box-shaped connector (female terminal **3**) again, as shown in FIG. **2**, the upper holder section **4** supports the push part **5** in a cantilever posture, and insertion of the male terminal **6** elastically deforms the push part **5**, whereby the reaction force to the deformation fixes the male terminal **6**. In FIG. **2**, denoted at **7** is the wire barrel part and denoted at **8** is the fixing segment. When such connectors are manufactured from a copper alloy material plate, bending and shear stamping are often used. For manufacturing of a small and precise connector, it is necessary to ensure an excellent bending formability in both the parallel direction and the perpendicular direction to the rolling direction. Upon creation of a big flash during shear stamping, the flash will get caught by the bent section and hinder precise bending, and if the flash is created in the wire barrel part, a wire will be severed during bending, and further, creation of any flash will promote abrasion of metal stamping dies. This is why this type of a copper alloy plate must exhibit an excellent bending formability and an excellent shear stamping workability.

**[0016]** The bending formability and the shear stamping workability of a conventional solid solution copper alloy mainly containing Cu—Ni—Sn on the other hand are still insufficient.

**[0017]** In light of these, the present invention aims at achieving a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction of a Cu—Ni—Sn—P alloy.

**[0018]** Another object of the present invention is to obtain a copper alloy plate made of a solid solution copper alloy mainly containing Cu—Ni—Sn for manufacturing of electric connection components which exhibits an excellent bending formability along the perpendicular and vertical direction to the rolling direction and also exhibits an excellent shear stamping workability.

**[0019]** To achieve these objects, in summary, a copper alloy exhibiting an excellent stress relaxation resistance according to the present invention is characterized in that it contains Ni: 0.1 through 3.0% (i.e., mass % which will be equally applied below), Sn: 0.01 through 3.0% and P: 0.01 through 0.3% and includes remainder copper and inevitable impurities, and in which the Ni content in extracted residues separated and left on a filter whose filter mesh size is 0.1 μm by an extracted residues method accounts for 40% or less of the Ni content in the copper alloy.

**[0020]** The extracted residues method requires that 10 g of the copper alloy is immersed in 300 ml of a methanol solution which contains 10 mass % of ammonium acetate, and using the copper alloy as the anode and platinum as the cathode, constant-current electrolysis is performed at the current density of 10 mA/$cm^2$, and the solution in which the copper alloy is thus dissolved is subjected to suction filtration using a membrane filter of polycarbonate whose filter mesh size is 0.1 μm, thereby separating and extracting undissolved residues on the filter.

**[0021]** Further, the Ni content in the extracted residues is identified through analysis by ICP after dissolving the undissolved residues separated and left on the filter into a solution prepared by mixing aqua regia and water at the ratio of 1:1.

**[0022]** In addition, to achieve these objects, a method of making a copper alloy plate exhibiting an excellent stress relaxation resistance according to the present invention is a method of making a plate of the copper alloy described in the summary above and preferred embodiments described later is characterized in that while a copper alloy plate is being made through casting of the copper alloy, hot rolling, cold rolling and annealing, the time needed until the start of casting since completion of addition of alloy elements to melting furnace is 1,200 seconds or shorter and the time needed until the end of hot rolling since ejection of an ingot from an ingot heating furnace is 1,200 seconds or shorter.

**[0023]** The copper alloy plate for use as electric connection components according to the present invention is characterized in that the copper alloy contains Ni: 0.4 through 1.6%, Sn: 0.4 through 1.6% and P: 0.027 through 0.15% and Fe: 0.0005 through 0.15%, the ratio Ni/P of the Ni content to the P content is lower than 15, the remainder part has Cu and impurities, the structure is that precipitates are dispersed in the of the copper alloy, the precipitates have diameters of 60 nm or smaller, and twenty or more precipitates having the diameters of 5 nm to 60 nm are observed within a scope of 500 nm×500 nm.

**[0024]** The composition of the copper alloy above may contain if necessary any one type or more of the elements Zn: 1% or less, Mn: 0.1% or less, Si: 0.1% or less and Mg: 0.3% or less, and/or Cr, Co, Ag, In, Be, Al, Ti, V, Zr, Mo, Hf, Ta and B in the total amount of 0.1% or less.

**[0025]** According to the present invention, a copper alloy mainly containing Cu—Ni—Sn—P exhibits a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction. It is also possible to obtain a copper alloy exhibiting excellent characteristics, such as the bending property, the electric conductivity (of about 30% IACS or more) and the strength (i.e., a proof stress of about 480 MPa or more), suitable as a terminal or connector.

**[0026]** The inventors of the present invention studied the reason why a conventional solid solution copper alloy in which precipitation of Ni—P compounds is suppressed described earlier almost exhibits a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the parallel direction to the rolling direction but fails achieving this along the perpendicular direction to the rolling direction.

**[0027]** As a result of the study, the inventors found that suppression of coarse oxides, crystalloids and precipitates of Ni having a certain size or larger would realize a high stress relaxation resistance which manifests itself as a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction.

[0028] In other words, coarse oxides, crystalloids and precipitates of Ni of a certain size or larger correspond to the amount of Ni in extracted residues separated and left on a filter whose filter mesh size is 0.1 μm referred to in the summary above of the present invention. If the Ni content in the extracted residues is suppressed down to 40% or less of the Ni content in the copper alloy described above, a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower is achieved along the perpendicular direction to the rolling direction. At the same time, an excellent bending property, an excellent electric conductivity and an excellent strength are attained.

[0029] Further, suppression of Ni compounds (Ni products) such as coarse oxides, crystalloids and precipitates of Ni having a certain size exceeding 0.1 μm makes it possible to ensure the amount of fine Ni compounds of 0.1 μm or smaller (including nano-level fine Ni clusters or finer Ni clusters), the amount of solute Ni in solid solutions (hereinafter referred to "solute Ni"), etc. A Ni cluster means a group of atoms as they are before crystallization when viewed at the atomic structure level.

[0030] Uniform and fine dispersion alone of Ni—P intermetallic compounds in the matrix of a Cu—Ni—Sn—P alloy according to Patent Document 1 does not make it possible to improve the stress relaxation resistance in the perpendicular direction to the rolling direction, and therefore, it is necessary to ensure the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni described above. However, it is not possible to directly measure fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni.

[0031] In contrast, the present invention is characterized in suppressing coarse Ni compounds of exceeding 0.1 μm described above and indirectly ensuring the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni.

[0032] To secure the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni while suppressing coarse Ni compounds of exceeding 0.1 μm described above in the present invention, different manufacturing conditions than those for an ordinary method are necessary. In short, as described in the summary above regarding the method of making a copper alloy plate according to the present invention, while a copper alloy plate is being made through casting of a copper alloy, hot rolling, cold rolling and annealing, it is necessary to shorten the time until the start of casting since completion of addition of alloy elements to melting furnace and the time until the end of hot rolling since ejection of an ingot from an ingot heating furnace.

[0033] At ordinary steps of manufacturing a copper alloy plate of this type, these required time periods tend to be long. Due to this, oxides and crystalloids created during melting and casting, and coarse precipitates created since soaking of an ingot until the end of hot rolling consume the most amount of the added Ni, thereby reducing the amount of fine Ni compounds of 0.1 μm or smaller and solute Ni expected to be created considering the amount of the added Ni, more than expected.

[0034] At ordinary steps of manufacturing a copper alloy plate of this type, it is normal to repeat hot rolling, cold rolling and annealing, thereby obtaining a final (product) plate while controlling the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni in accordance mainly with a cold rolling condition and an annealing condition. During this, dispersion of alloy elements such as Ni in appropriately dispersed intermetallic compounds stabilizes the amount of solute Ni and other elements and the amount of precipitation of fine products, which purpose is control of mechanical properties such as the strength level.

[0035] However, as described above, at these ordinary manufacturing steps, the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni measured in absolute amounts have already decreased through preceding steps. Hence, despite the effort to facilitate precipitation of the fine products mentioned above by means of a cold rolling condition and an annealing condition after hot rolling, the insufficient absolute amounts of the fine Ni compounds of 0.1 μm or smaller and solute Ni still make it difficult to improve the strength and the stress relaxation resistance.

[0036] Further, in the event that there are great amounts of coarse oxides, crystalloids and precipitates (Ni compounds) described above, these coarse products trap the fine products precipitated during cold rolling and annealing, which further reduces the fine products which are independently present in the matrix. With the ordinary manufacturing method described above therefore, it is not possible to achieve a sufficient strength and an excellent stress relaxation resistance although the amount of added Ni is large.

[0037] In contrast, according to the present invention, suppression of coarse Ni compounds of exceeding 0.1 μm described earlier makes it possible to secure the amount of necessary (useful) fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni. The consequence of this is a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction. At the same time, an excellent bending property, an excellent electric conductivity and an excellent strength are attained.

[0038] Further, it is possible according to the present invention to obtain electric connection components made of a solid solution copper alloy mainly containing Cu—Ni—Sn which exhibits an excellent bending formability along the perpendicular and vertical direction to the rolling direction and at the same time exhibits an excellent shear stamping workability.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0039] FIG. **1** shows cross sectional views for describing a stress relaxation resistance test on a copper alloy plate; and

[0040] FIG. **2** shows a front view (a) and a cross sectional view (b) of the structure of a box-shaped connector (female terminal).

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

### First Embodiment

[0041] (Chemical Composition of Copper Alloy)

[0042] First, the chemical composition of the copper alloy according to the present invention will be described. As described above, the premise with respect to the chemical composition of the copper alloy in the present invention is that the copper alloy is a Cu—Ni—Sn—P alloy which can be cast as an ingot in a shaft furnace therefore with high productivity at a greatly reduced cost.

[0043] In addition, to satisfy requirements for connection components such as automotive terminals and automotive connectors, namely, a high stress relaxation resistance along the perpendicular direction to the rolling direction, an excellent bending property, an excellent electric conductivity and an excellent strength, the copper alloy basically contains Ni:

0.1 through 3.0%, Sn: 0.01 through 3.0% and P: 0.01 through 0.3% and is made of remainder copper and inevitable impurities. The amounts of the respective elements expressed in % are all in percents by mass. The reason of adding or suppressing these alloy elements of the copper alloy will now be described.

**[0044]** (Ni)

**[0045]** Ni is an element which is necessary to create fine precipitates with P and improve the strength and the stress relaxation resistance. Even with the manufacturing method according to the present invention which is the most proper, the Ni content of less than 0.1% will result in an insufficient amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni measured as absolute amounts. Hence, the content must be 0.1% or more for the benefit of Ni to be felt effectively.

**[0046]** However, an excessive content beyond 3.0% will result in coarsening of Ni compounds such as oxides, crystalloids and precipitates of Ni or an increased amount of coarse Ni compounds, which will then lead to a failure of achieving the Ni content in the extracted residues of 40% or less of the Ni content in the copper alloy. This will reduce the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni. Further, since fracture will start at such coarsened Ni compounds, not only the strength and the stress relaxation resistance but the bending formability as well will deteriorate. For this reason, the Ni content is set within the range of 0.1 through 3.0%, or preferably 0.3 through 2.0%.

**[0047]** (Sn)

**[0048]** Sn dissolves as solid solutions in a copper alloy and enhances the strength. Further, Sn precipitates suppress recrystallization-induced softening during annealing. While annealing at a high temperature is necessary for positive creation of Sn precipitates in the copper alloy according to the present invention, if the Sn content is less than 0.1%, it is not possible to suppress recrystallization-induced softening during annealing, thus leading to a decreased strength. Hence, when the Sn content is less than 0.1%, the strength needs be enhanced by means of facilitated rolling reduction during final cold rolling after annealing or by otherwise appropriate approach. This however will slightly decrease the electric conductivity, the stress relaxation resistance, etc. Meanwhile, the Sn content of less than 0.01%, i.e., too little Sn, will result in too low a strength even despite enhanced rolling reduction during final cold rolling after annealing and make it impossible for the balance between these characteristics to achieve a desired level. On the contrary, the content over 3.0% will lower the electric conductivity and make it impossible to attain the electric conductivity of 30% IACS or higher. For this reason, the Sn content is set within the range of 0.01 through 3.0%, or preferably 0.1 through 2.0%, or more preferably 0.3 through 2.0%.

**[0049]** (P)

**[0050]** P is an element which is necessary to create fine precipitates with Ni and improve the strength and the stress relaxation resistance. The P content of less than 0.01% will result in a shortage of P-based fine precipitated particles, and hence, the content needs be 0.01% or more. An excessive content beyond 0.3% will however coarsen precipitated particles of Ni—P intermetallic compounds and deteriorate not only the strength and the stress relaxation resistance but the workability of hot working as well. For this reason, the Sn content is set within the range of 0.01 through 0.3%, or preferably 0.02 through 0.2%.

**[0051]** (Fe, Zn, Mn, Si, Mg)

**[0052]** Fe, Zn, Mn, Si and Mg can be easily mixed from materials for melting such as scraps. These elements, although respectively effective in some respects, generally decrease the electric conductivity. Further, higher contents of these will make ingot making difficult in a shaft furnace. Hence, to achieve the electric conductivity of 30% IACS or higher, Fe should be 0.5% or less, Zn should be 1% or less, Mn should be 0.1% or less, Si should be 0.1% or less and Mg should be 0.3% or less. In other words, any concentrations equal to or lower than these upper limits are acceptable in the present invention.

**[0053]** Like Sn, Fe increases the recrystallization temperature of a copper alloy. However, the Sn content exceeding 0.5% will decrease the electric conductivity and the electric conductivity of 30% IACS will not be achieved. The Sn content is preferably 0.3% or less.

**[0054]** Zn prevents spalling of a tin plating. The Zn content exceeding 1% however will decrease the electric conductivity and the electric conductivity of 30% IACS will not be achieved. For ingot making in a shaft furnace, the Zn content is preferably 0.05% or less. As long as Zn is used in a temperature range (approximately from 150 degrees Celsius to 180 degrees Celsius) for use as an automotive terminal, the Zn content of even 0.05% or less prevents spalling of a tin plating.

**[0055]** Mn and Si serve as deoxidizers. However, a content exceeding 0.1% will decrease the electric conductivity and the electric conductivity of 30% IACS will not be achieved. Further, for ingot making in a shaft furnace, it is desirable that the Mn content is 0.001% or less and the Si content is 0.002% or less.

**[0056]** Mg functions to improve the stress relaxation resistance. The Mg content exceeding 0.3% however will decrease the electric conductivity and the electric conductivity of 30% IACS will not be achieved. For ingot making in a shaft furnace, the Mg content is preferably 0.001% or less.

**[0057]** (Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au, Pt)

**[0058]** The copper alloy according to the present invention may contain additional elements of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in the total amount of 1.0% or less. Although preventing coarsening of crystal grains, these elements, when contained in the total amount which exceeds 1.0%, decrease the electric conductivity and the electric conductivity of 30% IACS can not be attained. This also makes ingot making in a shaft furnace difficult.

**[0059]** Other than these, 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 metals are impurities and should therefore be suppressed down to the total amount of 0.1% or less.

**[0060]** (Restriction on Extracted Residues)

**[0061]** As described above, the present invention suppresses coarse Ni oxides, crystalloids and precipitates (Ni compounds) which are larger than the 0.1-μm size and attains a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction.

**[0062]** In the context of the present invention, the amount of such coarse Ni compounds having this size or larger are defined as the Ni content in extracted residues separated and left on a filter whose filter mesh size is 0.1 μm. The Ni content in the extracted residues is regulated down to 40% or less of the Ni content in the copper alloy.

**[0063]** When the amount of coarse Ni compounds having the size mentioned above or larger is suppressed, the effect of securing the amount of fine Ni compounds of 0.1 μm or smaller, and the amount of solute Ni is added on top of the effect of suppressing such coarse Ni compounds. As a result, a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower is achieved along the perpendicular direction to the rolling direction. At the same time, an excellent bending property, an excellent electric conductivity and an excellent strength are attained.

**[0064]** If the proportion of the Ni content in the extracted residues in the Ni content in the copper alloy reaches or exceeds 40%, the amount of the coarse Ni compounds described above will increase. This will therefore result in an insufficient amount of fine Ni compounds of 0.1 μm or smaller and an insufficient amount of solute Ni. Hence, the stress relaxation resistance and the strength along the perpendicular direction to the rolling direction will decrease. Further, since fracture will start at these coarse compounds, the bending formability as well will deteriorate.

**[0065]** (Extracted Residues Method)

**[0066]** To ensure the reproducibility of measurement, specific measurement conditions are set for the extracted residues method according to the present invention. In short, the copper alloy weighting 10 g is immersed in 300 ml of a methanol solution which contains 10 mass % of ammonium acetate, and using the copper alloy as the anode and platinum as the cathode, constant-current electrolysis is performed at the current density of 10 $mA/cm^2$. The solution in which the copper alloy is thus dissolved is subjected to suction filtration using a membrane filter of polycarbonate whose filter mesh size is 0.1 μm, thereby separating and extracting undissolved residues on the filter. The filter mesh size of 0.1 μm of this filter is currently the finest filter mesh size.

**[0067]** In the solution in which the copper alloy is dissolved, solute Ni already existing in the copper matrix have been dissolved, while coarse Ni compounds larger than 0.1 μm and fine Ni compounds of 0.1 μm or smaller are dispersed without getting dissolved. Hence, the undissolved residues separated and left on the filter whose filter mesh size is 0.1 μm are only the coarse Ni compounds which are larger than 0.1 μm. Meanwhile, solute Ni dissolved in advance and the fine Ni compounds of 0.1 μm or smaller pass through the filter together with the solution.

**[0068]** (The Ni Content in Extracted Residues)

**[0069]** The Ni content in the residues thus extracted and separated is identified through analysis by ICP after dissolving the undissolved residues separated and left on the filter into a solution prepared by mixing aqua regia and water at the ratio of 1:1.

**[0070]** (Method of Making Copper Alloy)

**[0071]** The method of making the copper alloy according to the present invention will now be described. The process per se for making the copper alloy according to the present invention may be any ordinary method. In other words, a final (product) plate is obtained through repetition of casting a molten copper alloy whose chemical composition has been adjusted, facing of the surfaces of the resulting ingot, soaking, hot rolling, cold rolling and annealing. Control of the mechanical properties such as the strength level is achieved by means of controlled precipitation of fine products of 0.1 μm or smaller mainly in accordance with a cold rolling condition and an annealing condition.

**[0072]** However, the optimal method of making the copper alloy according to the present invention requires that during a stage of obtaining the copper alloy plate through copper alloy casting, hot rolling, cold rolling and annealing, the time since the completion of addition of the alloy elements into melting furnace until the start of casting is 1,200 seconds or shorter and that the time since ejection of an ingot from an ingot heating furnace until the end of hot rolling is 1,200 seconds or shorter.

**[0073]** To suppress coarse Ni compounds which are larger than 0.1 μm and secure the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni in the present invention, it is necessary to shorten the time since the completion of addition of the alloy elements into melting furnace until the start of casting and the time since ejection of an ingot from an ingot heating furnace until the end of hot rolling.

**[0074]** At ordinary steps of manufacturing a copper alloy plate of this type, these time periods tend to be long. This results in a state that oxides and crystalloids created during melting and casting, coarse precipitates created since ingot soaking until the end of hot rolling consume the most amount of the added Ni, thereby reducing the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni expected to be created considering the amount of the added Ni.

**[0075]** Due to this, even though one may try controlling the amount of fine Ni compounds of 0.1 μm or smaller and the amount of solute Ni later by means of mainly the cold rolling condition and the annealing condition at the later stage, the absolute amount of fine Ni compounds of 0.1 μm or smaller and the absolute amount of solute Ni have already been reduced at the preceding steps. Further, when there are a great amount of the coarse Ni compounds described above, the fine products precipitated during cold rolling and annealing will be trapped by these coarse products and the amount of the fine products independently present in the matrix will further decrease. With the ordinary manufacturing method described above therefore, it is not possible to obtain a sufficient strength and an excellent stress relaxation resistance despite a large amount of added Ni.

**[0076]** In light of this, according to the present invention, coarse Ni compounds are suppressed on the further upper stream side at the manufacturing steps. In short, particularly for suppression of coarse Ni compounds, it is important to control: (1) the time since the completion of addition of alloy elements into a melting furnace until the start of casting; and (2) the time since ejection of an ingot from a heating furnace until the end of hot rolling.

**[0077]** To be noted first, melting and casting per se may be performed by an ordinary method such as continuous casting and semi-continuous casting. However, in controlling (1) the time since the completion of addition of alloy elements into a melting furnace until the start of casting, casting completes preferably within 1,200 seconds or less since the completion of addition of the elements to the melting furnace, or more preferably, within 1100 seconds or less, and the cooling/solidification rate is preferably 0.1° C./sec or faster, or more preferably 0.2° C./sec or faster.

**[0078]** This makes it possible to suppress nucleation, growth and coarsening of oxides and crystalloids which contain Ni and to finely disperse the oxides and crystalloids. From the perspective of suppressed nucleation of oxides con-

taining Ni, it is more desirable that melting and casting is performed in vacuum or in an atmosphere in which the partial pressure of oxygen is low.

**[0079]** A time period of approximately 1,500 seconds or longer used to be required in order to melt without fail a mother alloy of Cu—P or the like containing additive elements, uniformly disperse within the molten alloy the additive elements which have dissolved as solid solutions, and to re-analyze after additionally loading the raw materials. The long time requires before casting however has been found to promote creation and coarsening of oxides containing Ni and lower the yield of the additive elements.

**[0080]** To avoid such creation and coarsening of oxides containing Ni, while making the copper alloy according to the present invention, the time since the completion of addition of alloy elements into a melting furnace until the start of casting is shortened preferably down to 1,200 seconds or shorter, or more preferably, to 1100 seconds or shorter. The shortening of the time required until casting can be achieved by predicting the composition as it is after additional loading of the raw materials from the past results of melting and by shortening the time necessary for re-analysis, etc.

**[0081]** To be noted next in controlling (2) the time since ejection of an ingot from the heating furnace until the end of hot rolling is the waiting time which the ingot removed from the heating furnace following heating in the furnace must wait for before the start of hot rolling. To make the copper alloy according to the present invention in which coarsening of Ni compounds is suppressed however, it is recommended to control both the time since melting until the start of casting and the cooling/solidification rate and to control the time (the total time elapsed) needed since ejection of the ingot from the heating furnace until the end of hot rolling down to 1,200 seconds or shorter, or more preferably, to 1100 seconds or shorter.

**[0082]** Such control of the time since ejection from a heating furnace until the end of hot rolling has never been studied before, leading to a common situation that a long time over 1,500 seconds is spent due to transportation from a heating furnace to a hot rolling line, a longer hot rolling time attributable to enlarged slabs which aim at improvement of the productivity. The required long period of time however has been found to result in precipitation of Ni-based coarse precipitates, and hence, precipitation of Ni and P around crystalloids and oxides created during melting and casting. Increase of such coarse precipitated particles will excessively increase the amount of Ni residues and therefore deteriorate the strength and the stress relaxation resistance.

**[0083]** To avoid reduction of solute Ni and coarsening of Ni compounds, while making the copper alloy according to the present invention, the total time required since ejection from a heating furnace until the end of hot rolling is actively controlled down to 1,200 seconds or shorter. Such time control can be attained by means of quick transportation of an ingot from the heating furnace to the hot rolling line and through use of a small slab rather than a large slab which will extend the hot rolling time.

**[0084]** Hot rolling may be performed by an ordinary method. The inlet temperature for hot rolling is from 600 to 1,000 degrees Celsius approximately, and the finishing temperature for hot rolling is from 600 to 850 degrees Celsius approximately. Hot rolling is followed by water cooling or standing for cooling.

**[0085]** Following this, cold rolling and annealing is performed, whereby a copper alloy plate or the like having the thickness as a product plate is made. Annealing and cold rolling may be repeated depending upon the thickness of the final (product) plate. As for cold rough rolling, the rolling reduction is selected so that the rolling reduction of approximately 30 through 80% will be obtained during final finishing rolling. Annealing for recrystallization may be performed in the middle of cold rough rolling as needed.

**[0086]** Annealing of the copper alloy plate as it is after cold rough rolling may be continuous annealing or batch annealing. To precipitate a large amount of fine Ni—P intermetallic compounds however, the holding temperature must naturally be high in the case of continuous annealing (which takes only a short time) but low in the case of batch annealing (which demands a long time). With respect to the processing temperature (actual temperature) and the holding time, 500-800° C.×10-60 seconds is preferable for continuous annealing and 300-600° C.×2-20 hours is preferable for batch annealing (long time). The annealing is preferably followed by rapid cooling at the cooling rate of 10° C./sec or faster.

**[0087]** Stress-relief annealing or stabilizing annealing after final finishing cold rolling is performed preferably at the actual temperature of 250 through 450 degrees Celsius for 20 through 40 seconds. This is because this will eliminate strain which has introduced during final finishing rolling but will not accompany softening of the materials or accordingly greatly reduce the strength.

## Second Embodiment

**[0088]** A copper alloy plate according to the second embodiment of the present invention will now be described. The composition of the copper alloy according to the second embodiment of the present invention will be described first.

**[0089]** Ni is an element which dissolves as solid solutions in the copper alloy, and accordingly enhances the stress relaxation resistance and improves the strength. However, when the Ni content is 0.4% or less, this effect is not promised, but the Ni content exceeding 1.6% will work with P, another additive element present at the same time, and easily precipitate intermetallic compounds, thereby reducing solute Ni and deteriorating the stress relaxation resistance. Hence, the Ni content is set to 0.4 through 1.6%. The range of 0.7 to 0.9% is more desirable.

**[0090]** Sn is an element which dissolves as solid solutions in the copper alloy and accordingly improves the strength due to work hardening. In the alloy system according to the second embodiment, this element serves also as an element which contributes to the heat resistance as well. While annealing at a high temperature is necessary for improvement of the bending formability and the shear stamping workability of the copper alloy plate according to the present invention, the Sn content of 0.4% or less will decrease the heat resistance and facilitate recrystallization-induced softening during annealing, and therefore result in failure of sufficiently increasing the annealing temperature. On the contrary, the Sn content exceeding 1.6% will lower the electric conductivity and the electric conductivity of 30% IACS will not be achieved in the copper alloy plate, namely, a final product. Noting this, the Sn content is set to 0.4 through 1.6%. The range of 0.6 to 1.3% is more desirable. High-temperature annealing brings about another advantage that a sufficient amount of solute Ni necessary for improvement of the stress relaxation resistance is secured.

**[0091]** P is an element which creates Ni—P precipitates at the manufacturing steps and accordingly improves the heat resistance during annealing. This makes it possible to perform annealing at a high temperature and improve the bending formability and the shear stamping workability. However, when the P content is less than 0.027%, P tends to combined with Ni which is added in a greater amount than the P content, and creates strong Ni—P intermetallic compounds, whereas addition of P in the amount exceeding 0.15% further increases the amount of precipitated Ni—P intermetallic compounds, either one of which fails to permit the Ni—P intermetallic compounds to dissolve again as solid solutions during annealing, leads to a deteriorated bending formability and a deteriorated shear stamping workability and results in a failure to secure enough solute Ni which are necessary to improve the stress relaxation resistance. Hence, the P content is set to 0.027 through 0.15%. 0.05 through 0.08% is more preferable.

**[0092]** The Ni/P ratio is set to 15 or smaller, to thereby improve the heat resistance owing to Ni—P precipitates for realizing dissolution of Ni as solid solutions and for pinning of dislocations in matrix at a high annealing temperature while at the same time ensuring decomposition and dissolution as solid solutions of the Ni—P precipitates during recrystallization-induced softening which is caused by annealing. When the Ni/P ratio is set to 15 or larger, the heat resistance becomes insufficient, and therefore, annealing must be performed at a relatively low temperature, the bending formability and the shear stamping workability do not improve and a sufficient stress relaxation resistance is not obtained.

**[0093]** Fe is an element which suppresses coarsening of recrystallized grains during annealing. Addition of Fe in the amount of 0.0005% or more to the copper alloy makes it possible to heat up the copper alloy to a high temperature during annealing, sufficiently dissolve the additive elements as solid solutions and at the same time suppress coarsening of recrystallized grains. The Fe content beyond 0.15% however will decrease the electric conductivity and the electric conductivity of 30% IACS will not be achieved.

**[0094]** The copper alloy according to the present invention may further contain accessory constituent of Zn, Mn, Mg, Si, etc.

**[0095]** Zn, preventing spalling of a tin plating, may be added in the amount of 1% or less. However, to the extent that Zn is used in a temperature range (approximately from 150 degrees Celsius to 180 degrees Celsius) for use as an automotive terminal, addition of Zn in the amount of even 0.05% or less is enough. For ingot making in a shaft furnace, the Zn content is preferably 0.05% or less.

**[0096]** Mn and Si may be added as deoxidizers, each in the amount of 0.01% or less. Mn and Si however are preferably added in the amount of 0.001% or less and in the amount of 0.002% or less, respectively.

**[0097]** Mg has a function of improving the stress relaxation resistance, and therefore, may be added in the amount of 0.3% or less. However, for ingot making in a shaft furnace, the Mg content is preferably 0.001% or less.

**[0098]** Cr, Co, Ag, In, Be, Al, Ti, V, Zr, Mo, Hf, Ta, B and the like prevent coarsening of crystal grains and may therefore be added in the amount of 0.1% or less all in total.

**[0099]** Pb is an impurity and should preferably be limited to 0.001% or less.

**[0100]** The structure of the copper alloy plate according to the present invention will now be described.

**[0101]** The copper alloy plate according to the present invention has a structure that precipitates of Ni—P intermetallic compounds are dispersed in the copper alloy. Of the precipitates, particles whose diameters are beyond 60 nm cause cracking during bending at small R/t (R: bend radius, t: plate thickness), and the presence if any of such particles will deteriorate the bending formability. In the event that the precipitated particles are not spherical, the diameters (lengths of the major axis) of the circumscribed circles of the precipitated particles are used as the diameters of precipitates referred to in the present invention.

**[0102]** Meanwhile, cracking starts at precipitates during shear stamping, and therefore, precipitates distributed at a high density realizes an excellent shear stamping workability. Fine precipitates whose diameters are smaller than 5 nm, in mutual interaction with dislocations, causes local work hardening in a shear stress field, and hence, finely dispersed precipitates whose diameters are 5 nm or longer, although contributing to propagation and progress of shear stamping, further improve the shear stamping workability and help reduce flashes since the fracture surface of shear stamping spreads through the locations of these precipitates. As for particles whose diameters are 60 nm or smaller which do not deteriorate the bending formability, it is desirable that there are on the average twenty such particles within the scope of 500 nm×500 nm and it is more desirable that there are thirty or more such particles.

**[0103]** The method of making the copper alloy plate according to the present invention will now be described.

**[0104]** The copper alloy plate according to the present invention can be made by performing hot rolling and cold rough rolling after homogenizing treatment of an copper alloy ingot, thereafter performing finishing continuous annealing of the copper alloy plate as it is after cold rough rolling, and further performing cold rolling and stabilizing annealing.

**[0105]** Since the copper alloy according to the present invention is not a precipitation hardened copper alloy and therefore does not require any particularly strict control of conditions during homogenizing treatment, hot rolling and cold rough rolling. For example, homogenizing treatment may be performed at 800 through 1,000 degrees Celsius for 0.5 to 4 hours, hot rolling may be performed at 800 through 950 degrees Celsius, and hot rolling may be followed by water cooling or standing for cooling. As for cold rough rolling, the rolling reduction is selected so that the rolling reduction of approximately 30 through 80% will be obtained during final finishing rolling. Annealing for recrystallization may be performed in the middle of cold rough rolling as needed.

**[0106]** On the contrary, finishing continuous annealing of the copper alloy plate as it is after cold rough rolling needs to be strictly controlled, for which purpose a proper holding temperature and an appropriate holding time must be set.

**[0107]** One principal feature of the alloy system defined in the present invention is that transition of the precipitated phase takes place during a few dozens of seconds of annealing over 650 degrees Celsius. As described earlier, if a holding temperature is low, relatively many coarse precipitates are observed. The thermodynamic principle is that a further increased holding temperature will usually further aggregate and coarsen precipitates. However, in the case of the alloy system according to the present invention, transition of the precipitated phase takes place from around 600 to 650

degrees Celsius: Coarse precipitates created in a low temperature region whose one end is a temperature near 600 to 650 degrees Celsius are decomposed and dissolve as solid solutions, and a new phase which precipitates fine Ni—P compounds appears. These precipitates contribute to improvement of the bending formability and reduction of stamping-induced flashes.

**[0108]** When a holding temperature is low, precipitated particles whose diameters exceed 60 nm tend to be observed, and meanwhile, in a composition area where the Ni content and the P content are very little, particles whose diameters are 60 nm or smaller fall short. Even at an annealing temperature beyond 650 degrees Celsius, if a holding time is short, decomposition and dissolution as solid solutions of coarse precipitates will become insufficient, fine precipitates will not be created easily, and precipitates whose diameters exceed 60 nm will be left. On the contrary, if the holding time is too long, recrystallized particles will become coarse, which could deteriorate the bending formability.

**[0109]** In the case of the composition of the copper alloy according to the present invention, high-temperature and short annealing held at a actual temperature exceeding 650 degrees Celsius for the period of 15 through 30 seconds makes it possible to obtain a structure in which precipitates of Ni—P intermetallic compounds are properly dispersed in the copper alloy. Annealing is preferably followed by rapid cooling at the cooling rate of 10° C./sec or faster.

**[0110]** The annealing temperature described above secured under this high-temperature/short condition promises another advantage that the precipitates of the Ni—P intermetallic compounds precipitated while the temperature rose dissolve as solid solutions and sufficient solute Ni needed for improvement of the stress relaxation resistance are obtained.

**[0111]** Stabilizing annealing after final finishing rolling is preferably performed at 250 through 450 degrees Celsius for 20 through 40 seconds. This is because this will eliminate strain which has introduced during final finishing rolling but will not accompany softening of the materials or accordingly greatly reduce the strength.

Example 1

**[0112]** Examples of the present invention will now be described. Various copper alloy thin plates made of Cu—Ni—Sn—P alloys in which the states of Ni compounds in the structures were different were made, and properties such as the strength, the electric conductivity and the stress relaxation resistance were evaluated.

**[0113]** Describing this more specifically, after making copper alloys whose chemical compositions are as shown in Table 1 each in a coreless furnace, ingot making by semi-continuous casting was performed, and ingots which were 70 mm thick, 200 mm wide and 500 mm long were obtained. The ingots were each rolled under the following common condition, thereby making the copper alloy thin plates. After facing of the surfaces of the ingots, hot rolling was performed, thereby obtaining plates which were 16 mm thick, which was followed by quenching in water from a temperature of 650 degrees Celsius or higher.

TABLE 1

| Category | Alloy Number | Chemical Composition of Copper Alloy Plate (remainder is Cu) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ni | Sn | P | Fe | Zn | Mn | Si | Mg | Other Elements Group A | Other Elements Group B |
| Examples of the Invention | 1 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 2 | 0.50 | 0.60 | 0.05 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 3 | 1.10 | 0.80 | 0.06 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 4 | 0.20 | 1.10 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 5 | 2.50 | 0.60 | 0.25 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 6 | 0.80 | 1.10 | 0.07 | 0.60 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 7 | 0.80 | 1.10 | 0.07 | 0.02 | 1.10 | 0.02 | 0.02 | 0.02 | — | — |
| | 8 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.12 | 0.02 | 0.02 | — | — |
| | 9 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.11 | 0.02 | — | — |
| | 10 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.4 | — | — |
| | 11 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 1.1 | — |
| | 12 | 0.80 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | 0.2 |
| | 13 | 0.80 | 0.04 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| Comparative Examples | 14 | 0.04 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 15 | 3.15 | 1.10 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 16 | 0.80 | 0.004 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 17 | 0.80 | 3.17 | 0.07 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 18 | 0.80 | 1.10 | 0.003 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |
| | 19 | 0.80 | 1.10 | 0.35 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | — | — |

Note:
1) The symbol "—" denotes that the content was at or below the detection limit.
2) Other Element Group A: Total content of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt
3) Other Element Group B: 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 Mish metals

**[0114]** Removal of oxidized scales from these plates was followed by cold rolling, continuous annealing, cold rolling and stress-relief annealing in this order, whereby the copper alloy thin plates were obtained. In other words, the plates as they were after primary cold rolling (cold rough rolling, intermediate cold rolling) were faced, and after annealing of the continuous type during which holding for 20 seconds at the actual temperature of 660 degrees Celsius was conducted, finishing cold rolling was performed at rolling reduction of 50%. The example 16 of the invention and the comparative example 19 alone shown in Table 2, due to an insufficient Sn content of less than 0.1%, failed to suppress annealing-in-

duced softening (recrystallization during annealing) and resulted in the weakened strength, and therefore, for these, rolling reduction during finishing cold rolling was raised up to a relatively high level of 80% in an attempt to improve the strength. This was followed by low temperature stress-relief annealing at the actual temperature of 400 degrees Celsius for 20 seconds, whereby the copper alloy thin plates were obtained which were 0.25 mm thick.

**[0115]** During this, as shown in Table 2, the time required since completion of addition of the alloy elements into a melting furnace until the start of casting (described as "TIME REQUIRED BEFORE THE START OF CASTING" in Table 2), the cooling/solidification rate during casting, the temperature upon ejection from a heating furnace, finishing temperature of hot rolling and the time required since ejection from the heating furnace until the end of hot rolling (described as "TIME REQUIRED BEFORE THE END OF HOT ROLLING" in Table 2) were varied, which controlled the states of Ni compounds in the structures of the copper alloy thin plates.

**[0116]** Test specimens weighting 10 g for measurement of extracted residues were taken out of thus obtained copper alloy thin plates, and by the method described earlier, the Ni contents in the extracted residues separated by meshes whose filter mesh size was 0.1 μm were identified through analysis by ICP described earlier. The proportions (%) of these in the Ni content in the copper alloys were then calculated. Table 2 shows the results.

TABLE 2

| Category | Number | Alloy Number | Time Required before the Start of Casting (sec) | Cooling/ Solidification Rate (° C./sec) | Temperature upon Ejection from Heating Furnace (° C.) | Finishing Temperature of Hot Rolling (° C.) | Time Required before the End of Hot Rolling (sec) |
|---|---|---|---|---|---|---|---|
| Examples of the Invention | 101 | 1 | 900 | 2 | 960 | 750 | 500 |
| | 102 | 1 | 1100 | 1 | 960 | 750 | 500 |
| | 103 | 1 | 900 | 2 | 930 | 650 | 800 |
| | 104 | 1 | 900 | 2 | 960 | 650 | 1150 |
| | 105 | 2 | 600 | 1 | 950 | 750 | 900 |
| | 106 | 3 | 1000 | 2 | 920 | 650 | 800 |
| | 107 | 4 | 900 | 2 | 960 | 750 | 500 |
| | 108 | 5 | 900 | 2 | 960 | 750 | 500 |
| | 109 | 6 | 900 | 2 | 960 | 750 | 500 |
| | 110 | 7 | 900 | 2 | 960 | 750 | 500 |
| | 111 | 8 | 900 | 2 | 960 | 750 | 500 |
| | 112 | 9 | 900 | 2 | 960 | 750 | 500 |
| | 113 | 10 | 900 | 2 | 960 | 750 | 500 |
| | 114 | 11 | 900 | 2 | 960 | 750 | 500 |
| | 115 | 12 | 900 | 2 | 960 | 750 | 500 |
| | 116 | 13 | 900 | 2 | 960 | 750 | 500 |
| Comparative Examples | 117 | 14 | 900 | 2 | 960 | 750 | 500 |
| | 118 | 15 | 900 | 2 | 960 | 750 | 500 |
| | 119 | 16 | 900 | 2 | 960 | 750 | 500 |
| | 120 | 17 | 900 | 2 | 960 | 750 | 500 |
| | 121 | 18 | 900 | 2 | 960 | 750 | 500 |
| | 122 | 19 | 900 | 2 | 960 | 750 | 500 |
| | 123 | 1 | 1300 | 2 | 960 | 750 | 500 |
| | 124 | 1 | 1500 | 2 | 960 | 750 | 500 |
| | 125 | 1 | 900 | 2 | 960 | 700 | 1300 |
| | 126 | 1 | 900 | 2 | 960 | 650 | 1900 |

| Category | Structure of Copper Alloy Plate | | Properties of Copper Alloy Plate | | | | |
|---|---|---|---|---|---|---|---|
| | Ni Content in Extracted Residues (%) | Proportion (%) of Ni Content in Extracted Residues in Ni Content in Alloy | Tensile Strength (MPa) | Yield Stress Corresponding to 0.2% (MPa) | Electric Conductivity (% IACS) | Stress Relaxation Ratio | Bendability |
| Examples of the Invention | 0.06 | 8 | 545 | 530 | 33 | 10 | ○ |
| | 0.10 | 13 | 540 | 525 | 35 | 13 | ○ |
| | 0.11 | 14 | 540 | 520 | 35 | 13 | ○ |
| | 0.18 | 23 | 535 | 520 | 38 | 14 | ○ |
| | 0.05 | 10 | 525 | 510 | 43 | 11 | ○ |
| | 0.20 | 18 | 540 | 520 | 39 | 13 | ○ |
| | 0.03 | 16 | 495 | 480 | 51 | 15 | ○ |
| | 0.75 | 30 | 515 | 500 | 30 | 15 | ○ |
| | 0.05 | 6 | 540 | 525 | 27 | 10 | ○ |
| | 0.06 | 8 | 545 | 535 | 25 | 10 | ○ |
| | 0.06 | 8 | 545 | 530 | 26 | 10 | ○ |
| | 0.06 | 8 | 540 | 525 | 26 | 10 | ○ |
| | 0.05 | 6 | 550 | 535 | 25 | 9 | ○ |
| | 0.06 | 8 | 550 | 530 | 25 | 11 | ○ |
| | 0.06 | 8 | 545 | 525 | 27 | 10 | ○ |
| | 0.06 | 8 | 490 | 475 | 38 | 16 | ○ |

TABLE 2-continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Comparative Examples | 0.004 | 10 | 485 | 470 | 34 | 20 | ○ |
| | 1.32 | 42 | 495 | 475 | 33 | 22 | X |
| | 0.06 | 8 | 460 | 445 | 40 | 17 | ○ |
| | 0.06 | 8 | 545 | 525 | 23 | 10 | ○ |
| | 0.03 | 4 | 480 | 460 | 35 | 18 | ○ |
| | 0.34 | 43 | 490 | 470 | 34 | 23 | X |
| | 0.03 | 41 | 520 | 500 | 40 | 21 | X |
| | 0.36 | 45 | 510 | 495 | 43 | 25 | X |
| | 0.34 | 43 | 515 | 495 | 42 | 23 | X |
| | 0.40 | 50 | 500 | 480 | 47 | 30 | X |

**[0117]** For each example, the test specimen was cut out from the copper alloy plate and subjected to a tensile test, electric conductivity measurement, stress relaxation ratio measurement and a bending test. Table 2 also shows these results.

**[0118]** (Tensile Test)

**[0119]** Test specimens were cut out from the copper alloy thin plates, and JIS5-tensile test specimens were made by machining so that the longitudinal direction of the test specimens became perpendicular to the rolling direction of the plate members Using an Instron-type universal testing machine of the type 5882, under the room temperature, at the test speed of 10.0 mm/min and with GL=50 mm, mechanical properties were measured. The yield stress is the tensile strength corresponding to permanent elongation of 0.2%.

**[0120]** (Electric Conductivity Test)

**[0121]** Specimens were taken from the copper alloy thin plates described above, and the electric conductivities were measured. As for the electric conductivities of the specimens of the copper alloy plates, strip-shaped test specimens which were 10 mm wide and 300 mm long were processed by milling the electric resistance values were measured using a double-bridge type resistance measurement machine in accordance with the method of measuring the electric conductivity of a nonferrous metal material defined in JIS-H0505, and the electric conductivities were calculated by an average cross sectional area size method.

**[0122]** (Stress Relaxation Property)

**[0123]** The stress relaxation rates of the copper alloy thin plates described above along the perpendicular direction to the rolling direction were measured, and the stress relaxation resistances along this direction were evaluated. To be more specific, test specimens were taken from the copper alloy thin plates described above and measured in a cantilever posture as shown in FIG. **1**. Strip-shaped test specimens **1** which were 10 mm wide (whose longitudinal direction was perpendicular to the rolling direction of the plate members) were cut out and fixed at their one ends to the rigid body test bench **2**, and deflection d (=10 mm) was applied upon the span-wise lengths L of the test specimens **1**. For this work, L was determined so that surface stress corresponding to 80% of the yield stress of the material would be applied upon the material. These were unloaded from an oven after held at 180 degrees Celsius in the oven for thirty hours, permanent strain **6** was measured after elimination of the deflection d, and the stress relaxation rates (RS) were calculated by $RS=(\delta/d)\times 100$. Calculated in terms of Larson-Miller's parameters, holding at 180 degrees Celsius for thirty hours approximately corresponds to holding at 150 degrees Celsius for 1,000 hours.

**[0124]** (Evaluation of Bending Workability)

**[0125]** The bending test of specimens of the copper alloy plates was conducted in accordance with the technical standard set by the Japan Copper and Brass Association. Plate members which were 10 mm wide and 30 mm high were cut out and bent in the GoodWay direction (i.e., with the bending axes directed perpendicular to the rolling direction) at the bend radius of 0.5 mm, and whether there were cracks in the bent sections was visually observed with an optical microscope of 50 magnifications. Those without any crack are denoted at the symbol "○", while those in which cracks were found are denoted at the symbol "X".

**[0126]** As Table 2 clearly shows, the examples 101 through 116 of the invention on the copper alloys (bearing the alloy numbers of 1 to 13) falling under the compositions according to the present invention described in Table 1 were made under preferable conditions of the time since the completion of addition of the alloy elements into the melting furnace until the start of casting of 1,200 seconds or less, the cooling/solidification rate of 0.5° C./sec or faster during casting and the time since ejection from the heating furnace until the end of hot rolling of 1,200 seconds or less. Further, both the temperature upon ejection from the heating furnace and the temperature at the end point of hot rolling were appropriate.

**[0127]** Hence, in the examples 101 through 116 of the invention in Table 2, Ni compounds, such as coarse oxides, crystalloids and precipitates of Ni of 0.1 μm or larger, were suppressed such that the proportions of the Ni contents in the extracted residues separated by the extracted residues method described earlier in the Ni contents in the copper alloys would be 80% or smaller. It is therefore inferred that the amounts of fine Ni compounds of 0.1 μm or smaller (including fine Ni clusters at the nano level or smaller Ni clusters), the amounts of solute Ni and the like were ensured.

**[0128]** The examples 101 through 116 of the invention thus each attained a high stress relaxation resistance represented by a stress relaxation ratio of 15% or lower along the perpendicular direction to the rolling direction. Further, exhibiting an excellent bending property and strength, these achieve superior properties for use in terminals, connectors, etc.

**[0129]** In comparing among the examples 101 through 116 of the invention in Table 2 however, the examples 102 and 106 which required a relatively long time since the completion of addition of the alloy elements into the melting furnace until the start of casting and the examples 103 and 104 which required a relatively long time since ejection from the heating furnace until the end of hot rolling exhibited relatively lower stress relaxation resistances than those attained by the examples 101 and 105 in which these time periods were relatively short.

**[0130]** Further, even among the examples 101 through 116 of the invention in Table 2, the examples 109 through 115 of the invention (bearing the alloy numbers of 6 to 12 in Table 1) in which the amounts of the other elements exceeded the preferable upper limits exhibited lower electric conductivities than the examples 101 through 108 of the invention.

**[0131]** In the examples 109 through 113 of the invention, Fe, Zn, Mn, Si and Mg were each in a great amount exceeding the preferable upper limits described earlier as denoted at the alloy numbers of 6 to 10 in Table 1.

**[0132]** In the example 114 of the invention, the total content of the elements Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt was large and exceeded the preferable upper limit of 1.0 mass % described earlier as denoted at the alloy number 11 in Table 1.

**[0133]** In the example 115 of the invention, 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 metals was large and exceeded the preferable upper limit of 1.0 mass % described earlier as denoted at the alloy number 12 in Table 1.

**[0134]** Meanwhile, in the example 116 of the invention covering the alloy 13 in Table 1, the Sn content was as low as less than 0.1%, and despite an attempt to improve the strength by setting rolling reduction during finishing cold rolling relatively high in the manner described earlier, annealing-induced softening made the stiffness relatively weak as compared to the other examples of the present invention.

**[0135]** On the contrary, in the comparative examples 123 through 126 shown in Table 2 covering the copper alloys (bearing the alloy number 1) falling under the compositions according to the present invention described in Table 1, the manufacturing conditions were nevertheless outside the preferable ranges.

**[0136]** In the comparative examples 123 and 124, the time required since the completion of addition of the alloy elements into the melting furnace until the start of casting was too long, exceeding 1,200 seconds. Meanwhile, in the comparative examples 125 and 126, the time since ejection from the heating furnace until the end of hot rolling was too long, exceeding 1,200 seconds.

**[0137]** Thus, in the comparative examples 123 through 126 shown in Table 2, the proportions of the Ni contents in the extracted residues separated by the extracted residues method described earlier in the Ni contents in the copper alloys exceeded 40%, and Ni compounds, such as coarse oxides, crystalloids and precipitates of Ni of 0.1 μm or larger, were too much and not suppressed. It is therefore inferred that the amounts of fine Ni compounds of 0.1 μm or smaller, the amounts of solute Ni and the like were not ensured.

**[0138]** In summary, the comparative examples 123 through 126 are remarkably inferior in terms of stress relaxation resistance along the perpendicular direction to the rolling direction to the examples of the present invention.

**[0139]** The comparative examples 117 through 122 shown in Table 2 used copper alloys not falling under the compositions according to the present invention denoted at the alloy numbers of 14 to 19 in Table 1. Hence, although the manufacturing conditions were within the preferable ranges, they were remarkably inferior to the examples of the present invention in terms of either the proportion of the Ni content in the extracted residues in the Ni content in the copper alloy, the stress relaxation resistance, the bending property, the electric conductivity or the strength.

**[0140]** The Ni content in the copper alloy according to the comparative example 117 was lower than the lower limit (denoted at the alloy number 14 in Table 1). Hence, the strength and the stress relaxation resistance were low.

**[0141]** The Ni content in the copper alloy according to the comparative example 118 was higher than the upper limit (denoted at the alloy number 15 in Table 1). Hence, the strength, the stress relaxation resistance and the bending formability were inferior.

**[0142]** The Sn content in the copper alloy according to the comparative example 119 was lower than the lower limit (denoted at the alloy number 16 in Table 1). Hence, in the comparative example 119, despite an attempt to improve the strength by setting rolling reduction during finishing cold rolling relatively high in the manner described earlier, annealing-induced softening made the strength too weak.

**[0143]** The Sn content in the copper alloy according to the comparative example 120 was higher than the upper limit (denoted at the alloy number 17 in Table 1). Hence, the electric conductivity was low.

**[0144]** The P content in the copper alloy according to the comparative example 121 was lower than the lower limit (denoted at the alloy number 18 in Table 1). Hence, the strength and the stress relaxation resistance were low.

**[0145]** The P content in the copper alloy according to the comparative example 122 was higher than the upper limit (denoted at the alloy number 19 in Table 1). Hence, the strength, the stress relaxation resistance and the bending formability were inferior.

**[0146]** The results above prove the validity of the chemical composition and the structure of the copper alloy plate according to the present invention and further the preferable manufacturing conditions for obtaining the structure, which aim at enhancing the strength and the electric conductivity and hence improving the stress relaxation resistance along the perpendicular direction to the rolling direction and the bending formability.

## Example 2

**[0147]** Examples of the copper alloy plate according to the second embodiment of the present invention will now be described.

**[0148]** Copper alloys covered with charcoal were molten in the atmosphere inside a Kryptol furnace, thereby obtaining ingots (No. 201 through No. 209) which were 45 mm thick and had the compositions shown in Table 3. After soaking at 965 degrees Celsius for three hours or 850 degrees Celsius for thirty minutes, hot rolling was performed, which made the ingots 15 mm thick, quenching (water cooling) was then performed from 830 degrees Celsius or a higher temperature, the both surfaces were thereafter faced 1 mm each, thereby obtaining the thicknesses of 13 mm, and cold rough rolling was conducted, whereby the thicknesses shown in Table 3 were obtained.

**[0149]** This was followed by finishing continuous annealing as for No. 201 through No. 208, while with respect to No. 209, batch-type intermediate annealing and annealing was performed with cold rolling interposed between the two, finishing cold rolling was then performed, and low temperature annealing (stabilizing annealing) was thereafter carried out. The conditions for the respective steps are as described in Table 3. The thickness of the final product plates was 0.25 mm.

TABLE 3

| No. | | Ni | Sn | P | Fe | Zn | Steps: Hot Rolling | Rough Rolling | Annealing Condition | Rolling Reduction for Finishing Rolloing | Low Temperature Annealing |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Examples | 201 | 0.82 | 1.19 | 0.073 | 0.018 | 0.021 | 965° C. × 30 min. →15 mm | →0.63 mm | 660° C. × 20 sec. | 60% | 400° C. × 20 sec. |
| | 202 | 0.71 | 1.18 | 0.046 | 0.11 | 0.021 | 965° C. × 30 min. →15 mm | →0.83 mm | 720° C. × 20 sec. | 70% | 400° C. × 20 sec. |
| | 203 | 0.62 | 0.52 | 0.054 | 0.019 | 0.022 | 965° C. × 30 min. →15 mm | →0.83 mm | 660° C. × 20 sec. | 70% | 400° C. × 20 sec. |
| | 204 | 1.02 | 0.52 | 0.092 | 0.019 | 0.022 | 965° C. × 30 min. →15 mm | →0.71 mm | 660° C. × 20 sec. | 65% | 400° C. × 20 sec. |
| Comparative Examples | 205 | 0.42 | 0.66 | 0.035 | 0.018 | 0.021 | 965° C. × 30 min. →15 mm | →0.83 mm | 550° C. × 20 sec. | 70% | 400° C. × 20 sec. |
| | 206 | 0.42 | 0.83 | 0.036 | 0.019 | 0.022 | 965° C. × 30 min. →15 mm | →0.83 mm | 600° C. × 20 sec. | 70% | 400° C. × 20 sec. |
| | 207 | 0.42 | 1.02 | 0.036 | 0.017 | 0.01 | 965° C. × 30 min. →15 mm | →0.63 mm | 550° C. × 20 sec. | 60% | 400° C. × 20 sec. |
| | 208 | 0.82 | 1.19 | 0.073 | 0.018 | 0.021 | 965° C. × 30 min. →15 mm | →0.63 mm | 600° C. × 20 sec. | 60% | 400° C. × 20 sec. |
| | 209 | 1.09 | 0.92 | 0.053 | 0.021 | 0.022 | 850° C. × 30 min. →15 mm | →1 mm | 500° C. × 2 hr. →0.72 mm 450 □ × 1 hr. | 67% | 400° C. × 20 sec. |

**[0150]** On each sample which was in the state of thus obtained final product, the electric conductivity, the strength, mechanical properties (tensile strength, yield stress and elongation), the spring elastic bending limit, the stress relaxation resistance, the bending formability and the shear stamping workability were measured as described below, and further, the distribution of precipitates was observed with a transmission electron microscope (TEM). Table 4 shows the results.

TABLE 4

| No. | | Electric Conductivity (% IACS) | Hv | Direction | Tensile Strength (N/mm$^2$) | Yield Stress (N/mm$^2$) | Elongation (%) | Bending Limit (N/mm$^2$) |
|---|---|---|---|---|---|---|---|---|
| | | Properties after Low Temperature Annealing | | | | | | |
| Examples | 201 | 33.1 | 175 | LD | 563 | 545 | 8.9 | 511 |
| | | | | TD | 539 | 527 | 9.2 | 551 |
| | 202 | 31.2 | 169 | LD | 538 | 521 | 10.1 | 500 |
| | | | | TD | 532 | 511 | 9.3 | 532 |
| | 203 | 44.4 | 167 | LD | 541 | 523 | 9.9 | 479 |
| | | | | TD | 530 | 511 | 8.1 | 541 |
| | 204 | 40.4 | 162 | LD | 532 | 516 | 9.5 | 503 |
| | | | | TD | 512 | 502 | 5.8 | 535 |
| Comparative Examples | 205 | 46.6 | 158 | LD | 506 | 488 | 9.8 | 454 |
| | | | | TD | 497 | 477 | 8.3 | 509 |
| | 206 | 43.1 | 160 | LD | 524 | 504 | 9.6 | 453 |
| | | | | TD | 503 | 482 | 7.8 | 503 |
| | 207 | 40.8 | 164 | LD | 523 | 501 | 9.3 | 476 |
| | | | | TD | 500 | 484 | 6.9 | 503 |
| | 208 | 34.5 | 175 | LD | 584 | 566 | 6.7 | 511 |
| | | | | TD | 579 | 565 | 6.2 | 551 |
| | 209 | 39.8 | 171 | LD | 530 | 516 | 7.6 | 448 |
| | | | | TD | 543 | 521 | 6.3 | 520 |

| No. | | Stress Relaxation Ratio (%) | W-Bending R/t = 2 | Average Flash Height (μm) | The Number of Precipitates Whose Diameters Exceed 60 nm | The Number of Precipitates Whose Diameter are from 5 nm to 60 nm |
|---|---|---|---|---|---|---|
| | | Properties after Low Temperature Annealing | | | Observation with TEM | |
| Examples | 201 | 11.4 | ○ | 6 | 0 | 61 |
| | | 13.2 | ○ | | | |

TABLE 4-continued

| | | | | | | |
|---|---|---|---|---|---|---|
| | 202 | 12.7 | ○ | 6 | 0 | 75 |
| | | 14.3 | ○ | | | |
| | 203 | 9.9 | ○ | 6 | 0 | 53 |
| | | 13.2 | ○ | | | |
| | 204 | 10.0 | ○ | 6 | 0 | 58 |
| | | 14.2 | ○ | | | |
| Comparative Examples | 205 | 13.3 | ○ | 11* | 0 | 6* |
| | | 21.0* | ○ | | | |
| | 206 | 13.7 | ○ | 12* | 0 | 8* |
| | | 26.6* | ○ | | | |
| | 207 | 18.1* | ○ | 13* | 0 | 9* |
| | | 29.0* | ○ | | | |
| | 208 | 13.4 | X* | 8 | 8* | 24 |
| | | 16.7* | X* | | | |
| | 209 | 13.1 | X* | 20* | 5* | 6* |
| | | 14.9 | X* | | | |

The symbol "*" denotes that the result is outside the range according to the invention or the property is inferior.

**[0151]** Electric Conductivity:

**[0152]** Measurement of the electric conductivity was in accordance with the method of measuring the electric conductivity of a nonferrous metal material defined in JIS-H0505, and the electric conductivities were measured by a four-terminal method using a double bridge.

**[0153]** Hardness:

**[0154]** Measurement of the hardness was in accordance with the micro-tensile test method defined in JIS-Z2251, and the Vickers hardness was measured with a test load of 100 g (0.9807 N).

**[0155]** Mechanical Properties:

**[0156]** JIS5-tensile test specimens were prepared by machining so that the longitudinal direction of the test specimens became parallel (LD) and perpendicular (TD) to the rolling direction of the plate members, and the mechanical properties were measured through a tensile test in accordance with JIS-Z2241. The yield stress is the tensile strength corresponding to permanent elongation of 0.2%.

**[0157]** Bending Limit:

**[0158]** Using a spring elastic bending limit testing machine manufactured by AKASHI (MODEL: APT), the bending limit was identified as a result of a moment-type test. The test direction of the material was set parallel (LD) and perpendicular (TD) to the rolling direction of the plate members.

**[0159]** Stress Relaxation Resistance:

**[0160]** The stress relaxation ratio was measured in a cantilever test as shown in FIG. **1**. Strip-shaped test specimens **1** which were 10 mm wide were cut out so that their longitudinal direction became parallel (LD) and perpendicular (TD) to the rolling direction of the plate members and the test specimens were fixed at their one ends to the rigid body test bench **2**, and a deflection d (=10 mm) was applied upon the span-wise lengths L of the test specimens **1**. For this work, L was determined so that surface stress corresponding to 80% of the yield stress of the material would be applied upon the material. These were unloaded from an oven after held at 180 degrees Celsius in the oven for thirty hours, permanent strain **6** was measured after elimination of the deflection d, and the stress relaxation rates (RS) were calculated by $RS=(\delta/d)\times 100$. Calculated in terms of Larson-Miller's parameters, holding at 180 degrees Celsius for thirty hours approximately corresponds to holding at 150 degrees Celsius for 1,000 hours.

**[0161]** Bending Formability:

**[0162]** Samples which were 10 mm wide and 35 mm long were cut out so that their longitudinal direction became parallel (LD) and perpendicular (TD) to the rolling direction of the plate members, and then nipped with a B-bending jig defined in the W-bending test of metallic materials in CESM0002 so that the bend lines became perpendicular to the longitudinal direction, and after W-bending at 90 degrees under a load of 1 ton at R/t=2 (R: bend radius, t: plate thickness) using a universal testing machine RH-30 manufactured by Shimadzu Corporation, whether there were cracks in the bent sections was evaluated, and those without any crack were marked "○", while those in which cracks were found were marked "X".

**[0163]** Shear Stamping Workability:

**[0164]** The circle stamping test complying with JCBAT310 (the method of a shearing test of a thin bar of copper and a copper alloy) set by the Japan Copper and Brass Association was conducted, measuring the shear-induced flash height. To be more specific, using a stamping press having the punch diameter of 10.000 mmϕ and the die diameter of 10.040 mmϕ, a circle was punched out from a sample coated in advance with the lubricant "Unipress PA-5" available from Nisseki Mitsubishi using a brush. The clearance of this stamping press was (one-side gap (the gap between the cutting blade of the die and the circumference of the punch)/the plate thickness of the sample)×100 (%))=8%, and the shear rate was 50 mm/min. Flashes created at the periphery of the punched circular hole were measured at four places which were apart from each other by 90 degrees around the circumference, and an average value was used as the flash height.

**[0165]** Observation of Precipitates Distribution:

**[0166]** Samples were finished into thin films for TEM observation, by an electro-polished thin film method (twin jet method). Using TEM H-800 (having the accelerating voltage of 200 kV) manufactured by Hitachi, Ltd., images were taken at 40,000 magnifications and 100,000 magnifications, and printed on photographic printing papers after further enlarged 1.5 times. The number of precipitates whose diameters were beyond 60 nm was counted in a square scope of 1,000 nm×1,000 nm on the photographic printing papers on which the images were magnified 60,000 times, and the number of precipitates whose diameters were from 5 nm to 60 nm was counted in a square scope of 500 nm×500 nm on the photographic printing papers on which the images were magnified

150,000 times. These were observed in multiple scopes and an average value was calculated. The precipitated particles above observed within the scopes were all spherical.

**[0167]** As Table 4 shows, No. 201 through No. 207 in which precipitates whose diameters were beyond 60 nm were not found were excellent in terms of bending formability along both the LD and the TD directions. With respect to No. 201 through 204 and No. 208 in which twenty or more precipitates whose diameters were from 5 nm to 60 nm were observed within the scopes of 500 nm×500 nm, the average flash height was low, and the flash height was particularly low in No. 201 through No. 204. Further, as for No. 201 through No. 204, the stress relaxation rates were 15% or lower along both the LD and the TD directions.

**[0168]** On the contrary, with respect to No. 205 through 207, although the small amounts of added Ni made it hard for coarse precipitates exceeding 60 nm to be created, since the annealing temperatures were low, transition to the new phase of fine precipitates which would take place around 650 degrees Celsius did not take place and the number of precipitated fine Ni—P compounds failed to reach a required count. The shortage of fine precipitates of 60 nm or smaller which would improve the shear property resulted in the flash height of beyond 10 μm and the inferior shear stamping workability. Since the amounts of added Ni were small, and additionally, since solute Ni present in the matrices were consumed by the precipitates, the amounts of solute Ni were not enough to maintain the stress relaxation resistances, and the stress relaxation rates were high (particularly in the TD direction).

**[0169]** As for No. 208, the annealing temperature was 600 degrees Celsius which was below 650 degrees Celsius, and therefore, coarse precipitates beyond 60 nm did not get decomposed sufficiently or became solid solutions again but were partially left remaining, which deteriorated the bending formability. Despite incomplete transition to the new phase of fine precipitates which would take place around 650 degrees Celsius, some fine precipitates were created due to the large amounts of added Ni, which suppressed the flash height low. In addition, since the total amount of Ni—P precipitates was great and the amount of Ni becoming solid solutions again was insufficient, it was not possible to ensure enough solute Ni needed for improvement of the stress relaxation resistance, and the stress relaxation rate was high along the TD direction.

**[0170]** With respect to No. 209, due to batch annealing under 650 degrees Celsius, precipitates remained as aggregation of 60 nm or larger. Although batch annealing was performed twice which realized perfect recrystallization, since a temperature which would decompose aggregations of precipitates and create fine precipitates was not reached, the bending formability deteriorated and the flash height was high.

**[0171]** As described above, it is possible according to the present invention to obtain a Cu—Ni—Sn—P alloy which exhibits a high stress relaxation resistance along the perpendicular direction to the rolling direction and which is excellent in strength, electric conductivity and bending formability. This permits application to connection components such as automotive terminals and automotive connectors which demand a favorable stress relaxation resistance along the perpendicular direction to the rolling direction.

**1**: A copper alloy with an excellent stress relaxation resistance comprising:

Ni: 0.1 through 3.0 mass %;

Sn: 0.01 through 3.0 mass %;

P: 0.01 through 0.3 mass %; and

remainder copper and inevitable impurities, and the Ni content in extracted residues separated and left on a filter having filter mesh size of 0.1 μm by using an extracted residues method accounting for 40 mass % or less of the Ni content in the copper alloy, wherein

said extracted residues method requires that 10 g of the copper alloy is immersed in 300 ml of a methanol solution which contains 10 mass % of ammonium acetate, and using the copper alloy as the anode and platinum as the cathode, constant-current electrolysis is performed at the current density of 10 $mA/cm^2$, and the solution in which the copper alloy is thus dissolved is subjected to suction filtration using a membrane filter of polycarbonate whose filter mesh size is 0.1 μm, thereby separating and extracting undissolved residues on said filter, and

the Ni content in said extracted residues is identified through analysis by ICP after dissolving said undissolved residues separated and left on said filter into a solution prepared by mixing aqua regia and water at the ratio of 1:1.

**2**: The copper alloy of claim **1**, further comprising:

Fe: 0.5 mass % or less;

Zn: 1 mass % or less;

Mn: 0.1 mass % or less;

Si: 0.1 mass % or less; and

Mg: 0.3 mass % or less.

**3**: The copper alloy of claim **1**, further comprising one or more elements selected from the group consisting of Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Au and Pt in the total amount of 1.0 mass % or less.

**4**: The copper alloy of claim **1**, further comprising one or more elements 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 metals in the total amount of 0.1 mass % or less.

**5**: A copper alloy comprising:

Ni: 0.4 through 1.6 mass %;

Sn: 0.4 through 1.6 mass %;

P: 0.027 through 0.15 mass %,

Fe: 0.0005 through 0.15 mass %; and

the remainder part having Cu and impurities, the ratio Ni/P of the Ni content to the P content being lower than 15, wherein

precipitates are dispersed in the copper alloy, and

said precipitates have diameters of 60 nm or smaller, and twenty or more precipitates having the diameters of 5 nm to 60 nm are observed within a scope of 500 nm×500 nm.

**6**: The copper alloy of claim **5**, further comprising one or more elements selected from the group consisting of:

Zn: 1 mass % or less;

Mn: 0.1 mass % or less;

Si: 0.1 mass % or less; and

Mg: 0.3 mass % or less.

**7**: The copper alloy of claim **5**, further comprising one or more elements selected from the group consisting of Cr, Co, Ag, In, Be, Al, Ti, V, Zr, Mo, Hf, Ta and B in the total amount of 0.1 mass % or less.

**8**: A copper alloy plate for electric connection components made of the copper alloy of claim **1**.

**9**: A method of making a copper alloy plate of the copper alloy of claim **1**, wherein while the copper alloy plate is being made through casting, hot rolling, cold rolling and annealing of the copper alloy, the time since the completion of addition

of alloy elements into melting furnace until the start of casting is 1200 seconds or shorter and the time since ejection of an ingot from an ingot heating furnace until the end of hot rolling is 1200 seconds or shorter.

**10**: A copper alloy plate for electric connection components made of the copper alloy of claim **5**.

* * * * *