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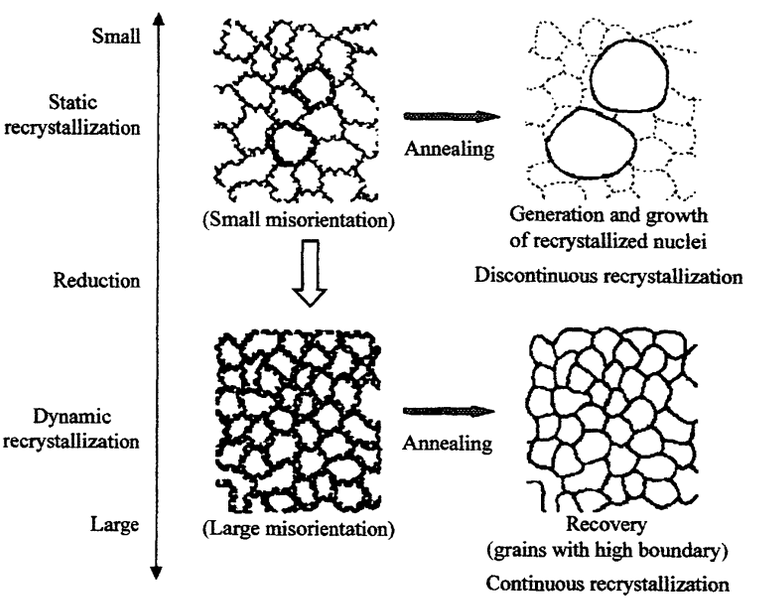
(54) Copper, copper alloy, and manufacturing method therefor

(57) Copper and copper alloy comprises: a structure having fine crystal grains with grain size of 1 μm or less after a final cold rolling with a reduction η, wherein η is expressed in the following formula and satisfying $\eta \geq 3$; and an elongation of 2% or more in a tensile test.

$$\eta = \ln (T_0/T_1)$$

T_0: plate thickness before rolling, T_1: plate thickness after rolling.

Fig. 1



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to copper and to copper alloys having fine crystal grains, and relates to a manufacturing method therefor, and more particularly, the resent invention relates to a technology for enhancing the characteristics in bending or other working when used for electronic devices such as terminals, connectors, and lead frames for semiconductor integrated circuits.

Description of the Related Art

[0002] Recently, electronic devices such as terminals and connectors and their parts are reduced in size and thickness, and copper and copper alloy used as materials thereof are demanded to have high strength. In terminal and connector material, the contact pressure must be increased in order to maintain electrical connections, and a high strength material is essential for this purpose. In a lead frame, because the semiconductor circuit is highly integrated, there is an increasing demand for multi-pin structures and thin wall thicknesses. Accordingly, to prevent deformation while conveying or handling the lead frame, the required strength level is progressively increasing.

[0003] Moreover, along with the trend in size-reduction of electronic devices and components, a higher degree of freedom of forming performance is demanded, and workability of connector materials is becoming important, and in particular, an excellent bending properties are required. In the outer lead of the semiconductor lead frame, an excellent bending properties are also needed in the case of gull-wing form bending processes.

[0004] In order to obtain an excellent bending properties not causing cracks in the bent part when a material is bent and deformed, it is necessary to enhance material ductility or to decrease grain size. Furthermore, for the copper alloy used for electronic device, a function for allowing the heat generated during power feed to escape to the outside is needed, aside from a function of transmitting an electric signal, and a high heat conductivity is required in addition to electrical conductivity. In particular, to cope with the recent trend of higher frequency electrical signals, the demand for higher electrical conductivity is mounting.

[0005] Electrical conductivity of copper alloy is inversely related to strength, and when an alloying element is added to enhance the strength, the electrical conductivity is lowered, and therefore alloys which compromise strength and electrical conductivity or price have been used, depending on the application. So far, alloys for enhancing the strength and electrical conductivity have been intensively developed, and generally, copper alloys of precipitation reinforced type containing second phase particles such as Cu-Ni-Si alloy or Cu-Cr-Zr alloy have come to be used as high functional materials which is superior in balance between both.

[0006] Thus, for mechanical characteristics of copper or copper alloys for electronic devices, high strength and excellent workability are desired. However, first of all, strength and ductility are inversely related to each other, and in each alloy system, when rolling is processed in order to increase the strength by work hardening, the ductility declines, and preferable workability is not obtained by rolling alone. On the other hand, by reducing the grain size, increase in strength as indicated by the Hall-Petch relation is expected, and it also leads to improvement of bending properties, and hence it was generally controlled to reduce the grain size during annealing and recrystallization.

[0007] In this method, however, when the annealing temperature is lowered in order to reduce the grain size, non-crystallized grains remain in part, and there is substantially a limit to obtaining recrystallized grains of about 2 to 3 μm, and a technique for further reducing the grain sizes has been demanded. Furthermore, by recrystallization alone, the strength level is usually low, and it is not practical, and therefore a certain rolling process is needed in a later step, which has led to reduction of ductility. Accordingly, generally after rolling process, a process of stress relief annealing was needed to recover the ductility. This process, however, causes lowered strength once obtained in the rolling process, and sufficient ductility is not obtained after stress relief annealing, and it was difficult to satisfy the recent extremely severe demand for bending deformation performance.

[0008] More recently, instead of an annealing process, methods of obtaining fine crystal grains and high ductility by working materials by strong shearing have been studied and reported, for example, by Ito et al. (ARB (Accumulative Roll-Bonding, J. of Japan Society of Metallurgy, 54 (2000), 429), and Hotta et al. (ECAP (Equal-Channel Angular Press), Metallurgy seminar text: Approach to fine crystal grains (2000), Japan Society of Metallurgy, 39). In these processing methods, however, a mass quantity sufficient to be used as materials for electronic devices cannot be manufactured, and there are not suited to industrial production.

SUMMARY OF THE INVENTION

[0009] The inventors have accumulated extensive research to solve these problems, and they have discovered that fine crystal grains at a level not known thus far can be obtained by controlling the conditions of the rolling process instead of the conditions of the annealing. That is, in the structure of a material cold rolled with an ordinary cold rolling reduction, when recrystallized by subsequent annealing, the decrease in dislocation density occurs discontinuously when the recrystallized grain boundaries pass a cell, and large crystal grains of uneven size are produced intermittently. This is called static recrystallization. According to the research by the inventors, by extremely increasing the reduction of cold rolling, dynamic recrystallization, usually exhibited in high temperature regions, was also found to occur in cold rolling, and dynamic continuous recrystallization is exhibited as the subgrains formed during processing are transformed into high angle grain boundaries. By making use of this mechanism, round and uniform crystal grains of grain size of 1 μm or less are obtained. According to this method, fine crystal grains can be obtained without sacrificing the strength in order to prevent reduction of ductility, and it is also found that an elongation of 2% or more is obtained even immediately after final cold rolling, and an allowable bending properties are obtained by cold rolling alone. Furthermore, by adding stress relief annealing processing after final cold rolling, the elongation is further enhanced, and thus is applicable also in the case exposed to extremely severe bending. According to such a manufacturing method, moreover, materials for electronic devices can be mass produced industrially. Continuous recrystallization is explained in detail below.

[0010] The present invention is made on the basis of these findings, and provides copper and copper alloy comprising: a structure having fine crystal grains with grain size of 1 μm or less composed of crystal grain boundaries mainly formed of curved portions after a final cold rolling, the structure obtained by dynamic continuous recrystallization caused by the final cold rolling, and an elongation of 2% or more in a tensile test.

[0011] The present invention also provides a manufacturing method for copper and copper alloy, the method comprising: a final cold rolling with a reduction (true stress) η, wherein η is expressed in the following formula and satisfying $\eta \geq 3$, thereby obtaining a structure having fine crystal grains with grain size of 1 μm or less after the final cold rolling, and an elongation of 2% or more in a tensile test.

$$\eta = \ln (T_0/T_1)$$

T_0: plate thickness before rolling, T_1: plate thickness after rolling.

[0012] The reasons for setting these numerical values are explained below together with the functions of the invention.

A. Reduction of final cold rolling, elongation, and grain size

[0013] In order to obtain a favorable bending properties in a material subjected to final cold rolling alone, a high ductility is essential. In order to obtain the favorable bending properties not causing cracking in the bent portion, a fracture elongation in a tensile test is required to be 2% or more at a gauge length of 50 mm. In order to obtain a rupture elongation of 2% or more in the state of final cold rolling, the grain size after final cold rolling must be 1 μm or less. Thus, sufficient elongation is obtained in the cold rolled state by decreasing the grain size, which is because dislocations are piled-up in the grain boundary when continuous recrystallized grains are formed, and a grain boundary structure of a non-equilibrium state is formed and a grain boundary sliding is expressed, thereby enhancing the ductility.

[0014] The grain size and elongation after final cold rolling vary depending on the cold rolling reduction. The cold rolling reduction (true stress) η by final cold rolling process until reaching the product plate thickness is expressed in the formula below.

$$\eta = \ln (T_0/T_1)$$

T_0: plate thickness before rolling, T_1: plate thickness after rolling.

[0015] In this case, when the value of η is small, a rolled structure remains, and clear fine crystal grains are not obtained, or if they are obtained, the grain size is large, and the grain boundary sliding does not take place, and favorable ductility is not obtained. According to the research by the inventors, it is known that the value of η should be 3 or more in order to obtain a fine grain size of 1 μm or less.

[0016] The structure of a material cold rolled by a conventional ordinary cold rolling reduction sometimes had a cell structure due to mutual entangling of dislocations introduced in the crystal grains. In this case, however, since the misorientation among neighboring cells is small, that is, 15° or less, properties as crystal grain boundary are not real-

ized. Accordingly, as shown in Fig. 1, when recrystallized by annealing after cold rolling, as mentioned above, static crystallization takes place, that is, large crystal grains of uneven size are formed intermittently.

[0017] In contrast, by setting the extremely high cold rolling reduction, fine crystal grains are obtained. That is, at a very high cold rolling reduction, numerous regions locally shearing deformed occur in the matrix in the entire material and thus subgrain structures greatly grow. As a result, as shown in Fig. 1, dislocations are introduced in order to compensate the large misorientation between the matrix and the subgrain, and they are piled-up in the grain boundary. In this case, crystal grain boundaries having a large misprientation of 15° or more (high angle grain boundary) are generated. That is, the subgrain structure which has been initially a substructure of crystal grains is directly formed as crystal grains. In this case, the crystal grain boundary is largely different from the case of the static recrystallization, and there is no linearity in the grain boundary, and it is a feature that a crystal grain boundary mainly composed of curved portions is formed. This dynamic continuous recrystallization is mostly formed in cold rolling. It is also known that a clearer high angle grain boundary is grown by annealing at intentional low temperatures and bringing it into an ordinary recovery regime. In this case, it is found that the ductility is further enhanced as described below.

[0018] In this mechanism, if second phase particles such as precipitates and dispersoids are present in the Cu matrix, dislocations introduced by plastic stress due to rolling are accumurated around the second phase particles by forming dislocation loops or the like, and the dislocation density is substantially increased. In this condition, the particle size of the subgrains becomes much finer, and the strength becomes higher. In the final cold rolling, unless recovered or recrystallized by annealing in an intermediate processing, cold rolling may be performed by plural rolling machines by exchanging rolling machines depending on the range of plate thickness, or pickling or polishing may be performed in order to control the surface properties.

B. Stress relief annealing

[0019] When the material after final cold rolling is further annealed for stress relief, the ductility is enhanced, and a further preferable bending properties are obtained. As annealing conditions, it is necessary to set adequate annealing conditions to such an extent that the product value will not be lost due to extreme decline of strength. The annealing condition differs with the alloy system, but by selecting an appropriate annealing condition in a temperature range of 80 to 500°C and in a range of 5 to 60 minutes, an elongation of 6% or more may be easily obtained, and it is applicable to a severe bend forming.

[0020] Preferred examples of copper alloy of the invention include Cu-Ni-Si alloys having precipitates of intermetallic compounds of Ni and Si such as Ni_2Si, and the copper alloys comprise Ni: 1.0 to 4.8 mass %, Si: 0.2 to 1.4 mass %, and the balance of Cu. The invention also includes Cu-Cr-Zr alloys having precipitates of pure Cr grains and intermetallic compounds of Cu and Zr, and the copper alloys comprise Cr: 0.02 to 0.4 mass %, Zr: 0.1 to 0.25 mass %, and balance of Cu. These copper alloy may be added with subsidiary components such as one or more of Sn, Fe, Ti, P, Mn, Zn, In, Mg and Ag in a total amount of 0.005 to 2 mass %. Moreover, copper alloys having second phase particles such as other kinds of precipitates and dispersed particles may be used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

Fig. 1 is a schematic diagram for explaining the recrystallization process.

Fig. 2 is a transmission electron microscope photograph showing a structure of an alloy in an example of the invention.

Fig. 3 is a transmission electron microscope photograph showing a structure of an alloy in a comparative example of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Embodiments)

[0022] Effects of the invention are more specifically described below by referring to preferred embodiments. First, using electric copper or oxygen-free copper as material, a specified amount of the material was put in a vacuum melting furnace, together with other additive elements, if necessary, and ingots of the chemical composition shown in Tables 1 to 3 were obtained by casting at the molten metal temperature of 1250°C. Table 1 shows the compositions of Cu-Ni-Si alloys, Table 2 shows the Cu-Cr-Zr alloys, and Table 3 shows other copper alloys.

Table 1

Cu-Ni-Si alloy

		Chemical composition			Final Rolling Condition			Product Properties			
		Ni	Si	Cu and Impurities	Original Plate Thickness (mm)	Final Plate Thickness (mm)	Cold Rolling Reduction	Grain Size (μm)	Tensile Strength (MPa)	Rupture Elongation (%)	Bending Properties	Conductivity (% IACS)
Example of Invention	1	3.02	0.67	Balance	3.30	0.15	3.1	0.20	820	3.7	○	48
	2	2.75	0.59	Balance	3.80	0.15	3.2	0.15	810	3.8	○	50
	3	3.18	0.62	Balance	3.65	0.15	3.2	0.15	830	4.5	○	49
	4	3.30	0.70	Balance	3.40	0.15	3.1	0.20	820	3.8	○	48
	5	2.60	0.55	Balance	3.00	0.15	3.0	0.40	800	2.3	○	51
Comparative Example	6	3.21	0.59	Balance	1.85	0.15	2.5	2.00	800	1.2	×	48
	7	2.80	0.58	Balance	1.10	0.15	2.0	Rolled Structure	790	0.8	×	50
	8	3.15	0.64	Balance	2.50	0.15	2.8	1.35	800	1.8	×	47

Table 2

Cu-Cr-Zr alloy

		Chemical Composition				Final Rolling Condition			Product Properties			
		Cr	Zr	Zn	Cu and Impurities	Original Plate Thickness (mm)	Final Plate Thickness (mm)	Cold Rolling Reduction	Grain Size (μm)	Tensile Strength (MPa)	Rupture Elongation (%)	Bending Properties	Conductivity (%IACS)
Example of Invention	9	0.21	0.08	–	Balance	3.25	0.15	3.1	0.30	610	3.5	○	80
	10	0.18	0.10	–	Balance	3.50	0.15	3.1	0.30	600	3.9	○	82
	11	0.23	0.14	–	Balance	3.80	0.15	3.2	0.25	620	4.8	○	79
	12	0.18	0.07	0.22	Balance	3.75	0.15	3.2	0.25	610	5.0	○	78
	13	0.24	0.11	0.18	Balance	3.10	0.15	3.0	0.35	620	2.8	○	77
Comparative Example	14	0.20	0.11	–	Balance	1.15	0.15	2.0	Rolled Structure	590	0.8	×	80
	15	0.18	0.08	–	Balance	2.60	0.15	2.9	1.20	600	1.7	×	81
	16	0.23	0.09	0.19	Balance	1.50	0.15	2.3	1.40	590	1.3	×	78

Table 3

Manufacturing conditions of other alloys of the invention and comparative examples

		Chemical Composition (w%)														Final Rolling Condition		
		Sn	Cr	Zr	Ni	Si	Fe	Ti	P	Mn	Zn	In	Mg	Ag	Cu and Impurities	Original Plate Thickness (mm)	Final Plate Thickness (mm)	Cold Rolling Reduction
Example of Invention	17	—	—	—	—	—	—	—	—	—	—	—	—	—	Tough Pitch Copper	3.80	0.15	3.2
	18	—	—	—	—	—	—	—	—	—	—	—	—	—	Oxygen-free Copper	3.40	0.15	3.1
	19	—	—	—	—	—	—	—	—	—	—	—	—	0.03	Balance	3.50	0.15	3.1
	20	5.12	—	—	—	—	—	—	0.02	—	—	—	—	—	Balance	3.10	0.15	3.0
	21	—	0.18	—	—	—	—	—	—	—	—	—	—	—	Balance	3.25	0.15	3.1
	22	0.22	0.28	—	—	—	—	—	—	—	0.19	—	—	—	Balance	3.75	0.15	3.2
	23	—	—	0.08	—	—	—	—	—	—	—	—	—	—	Balance	3.65	0.15	3.2
	24	—	0.18	0.11	—	—	0.61	0.37	—	—	—	—	—	—	Balance	3.00	0.15	3.0
	25	—	0.22	0.13	—	—	—	—	—	—	—	0.04	—	—	Balance	3.10	0.15	3.0
	26	—	0.26	0.11	—	0.02	—	—	—	—	—	—	0.04	—	Balance	3.75	0.15	3.2
	27	—	—	—	2.61	0.51	—	—	—	—	0.29	—	—	—	Balance	3.70	0.15	3.2
	28	0.51	—	—	2.11	0.48	—	—	—	—	0.48	—	—	—	Balance	3.65	0.15	3.2
	29	—	—	—	—	—	1.81	—	0.15	—	—	—	0.02	—	Balance	3.30	0.15	3.1
	30	—	—	—	—	—	2.43	—	0.03	—	0.12	—	—	—	Balance	3.75	0.15	3.2
	31	—	—	—	—	0.04	3.01	—	0.26	0.03	—	—	—	—	Balance	3.80	0.15	3.2
	32	—	—	—	—	—	—	2.95	—	—	—	—	—	—	Balance	3.50	0.15	3.1
Comparative Example	33	—	0.18	0.09	—	—	—	—	—	—	0.12	—	—	—	Balance	1.10	0.15	2.0
	34	—	—	—	3.12	0.67	—	—	—	—	0.14	—	—	—	Balance	2.50	0.15	2.8

[0023] These ingots were hot rolled at a temperature of 950°C into plates of 10 mm in thickness. The oxide layer of the surface layer was removed by mechanical scalping, and the plates were cold rolled to a thickness of 5 mm, and a solid solution treatment was applied in the case of age precipitation type copper alloy, and recrystallization annealing was applied once in the others. By further cold rolling, plates of an intermediate thickness of 1.1 to 3.8 mm were obtained, and at this plate thickness, further, aging treatment or second recrystallization annealing was performed. In the case of aging treatment, the aging temperature was adjusted so that the product strength would be highest in each alloy composition, or in the case of recrystallization, the temperature condition was adjusted so that the grain size would be 5 to 15μm. By the final cold rolling, plates of 0.15 mm in thickness were manufactured and obtained as experiment samples for evaluation. The final cold rolling conditions are also shown in Tables 1 to 3.

[0024] Test pieces were sampled from the obtained plates, and the materials were tested to evaluate "grain size", "strength", "elongation", "bending", and "electrical conductivity". To evaluate the "grain size", the bright fields were observed by a transmission electron microscope, and it was determined by the cut-off method of JIS H 0501 on the obtained photograph. As for "strength" and "elongation", using No. 5 specimens conforming to the tensile test specified in JIS Z 2241, the tensile strength and rupture elongation were measured. As for "bending", by bend forming using a W-bend testing machine, the bent part was observed by an optical microscope at a magnification of 50 times, and presence or absence of cracking was observed. The mark "o" indicates that cracking is absent, and the mark "x" indicates that cracking is present. The "electrical conductivity" was determined by measuring the electrical conductivity according to a four-point method.

[0025] Evaluation results are shown in Tables 1, 2, and 4. The alloys of the invention are known to have excellent strength, elongation and bending properties. By contrast, in comparative examples 6 to 8, 14 to 16, 33, and 34, since the reduction of final rolling was low, the desired structure was not obtained, the ductility dropped, and favorable bending properties were not achieved. Fig. 2 is a transmission electron microscope photograph of sample No. 12 of the invention, in which the mean grain size of the formed continuous recrystallization is 1 μm or less, and its crystal grain boundary is mainly composed of curved portions and is round. By way of comparison, a transmission electron microscope photograph of comparative example No. 6 is shown in Fig. 3, in which the grain size is nearly linear.

[0026] The materials manufactured in embodiments 9, 22, 26, and 30 of the invention and comparative examples 33, and 34 were further annealed for stress relief, and tensile tests were conducted. Results are shown in Table 5. In the alloys of the invention, by stress relief annealing, elongation is further enhanced as compared with that of the alloys of the comparative examples. Hence, it is expected to be able to withstand further more severe working.

Table 4

Characteristic evaluation results of alloys of the invention and comparative examples

		Grain size (μm)	Tensile strength (MPa)	Rupture elongation (%)	Bending Properties	Conductivity (%IACS)
Example of Invention	17	0.40	420	2.5	○	100
	18	0.45	410	2.7	○	100
	19	0.30	420	2.8	○	98
	20	0.25	630	2.1	○	15
	21	0.45	590	2.9	○	78
	22	0.35	610	2.2	○	74
	23	0.25	550	3.6	○	87
	24	0.15	670	2.3	○	69
	25	0.30	580	3.8	○	80
	26	0.30	590	3.9	○	52
	27	0.15	790	3.6	○	50
	28	0.20	780	2.6	○	52
	29	0.35	570	2.9	○	60
	30	0.20	540	2.5	○	63
	31	0.35	590	2.8	○	56
	32	0.40	1020	2.4	○	11
Comparative Example	33	Rolled Structure	590	1.2	×	80
	34	1.35	800	0.9	×	50

Table 5

Characteristic evaluation results after stress relief annealing

Alloy name			Stress Relief Annealing Conditions		Tensile Strength (MPa)	Rupture Elongation (%)	Conductivity (%IACS)
			Temperature(℃)	Time (min)			
Example of Invention	9		400	15	570	8.2	82
	22		400	15	590	8.9	75
	26		450	15	740	9.5	52
	30		400	15	520	7.5	65
Comparative Example	33		400	15	570	5.1	81
	34		450	15	740	4.5	50

Claims

1. Copper and copper alloy comprising:

   a structure having fine crystal grains with grain size of 1 μm or less composed of crystal grain boundaries mainly formed of curved portions after a final cold rolling, the structure obtained by dynamic continuous re-crystallization caused by the final cold rolling, and
   an elongation of 2% or more in a tensile test.

2. Copper and copper alloy comprising:

   a structure having fine crystal grains with grain size of 1 μm or less after a final cold rolling with a reduction η, wherein η is expressed in the following formula and satisfying $\eta \geq 3$; and
   an elongation of 2% or more in a tensile test.

$$\eta = \ln (T_0/T_1)$$

   T_0: plate thickness before rolling, T_1: plate thickness after rolling.

3. A manufacturing method for copper and copper alloy, the method comprising:

   a final cold rolling with a reduction η, wherein η is expressed in the following formula and satisfying $\eta \geq 3$, thereby obtaining a structure having fine crystal grains with grain size of 1 μm or less after the final cold rolling, and
   an elongation of 2% or more in a tensile test.

$$\eta = \ln (T_0/T_1)$$

   T_0: plate thickness before rolling, T_1: plate thickness after rolling.

4. A manufacturing method for copper and copper alloy according to claim 3, wherein the copper and copper alloy recited in claim 1 or 2 is processed by strain relieving annealing, and elongation by a tensile test is improved to 6% or more.

5. Copper and copper alloy manufactured by the manufacturing method of claim 3 or 4.

6. A manufacturing method of copper and copper alloy according to claim 3 or 4, wherein the copper alloy is Cu-Ni-Si alloy or Cu-Cr-Zr alloy.

7. Copper and copper alloy of claim 5, wherein the copper alloy is Cu-Ni-Si alloy or Cu-Cr-Zr alloy.

Fig. 1

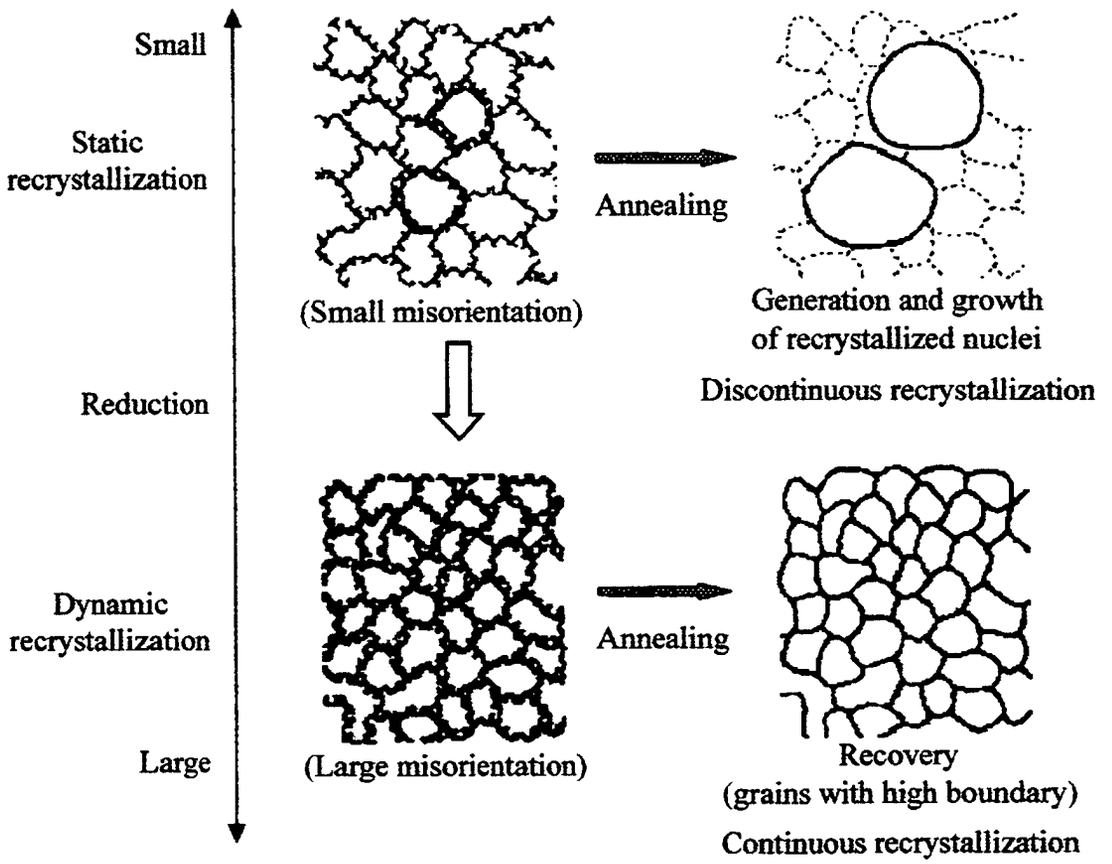
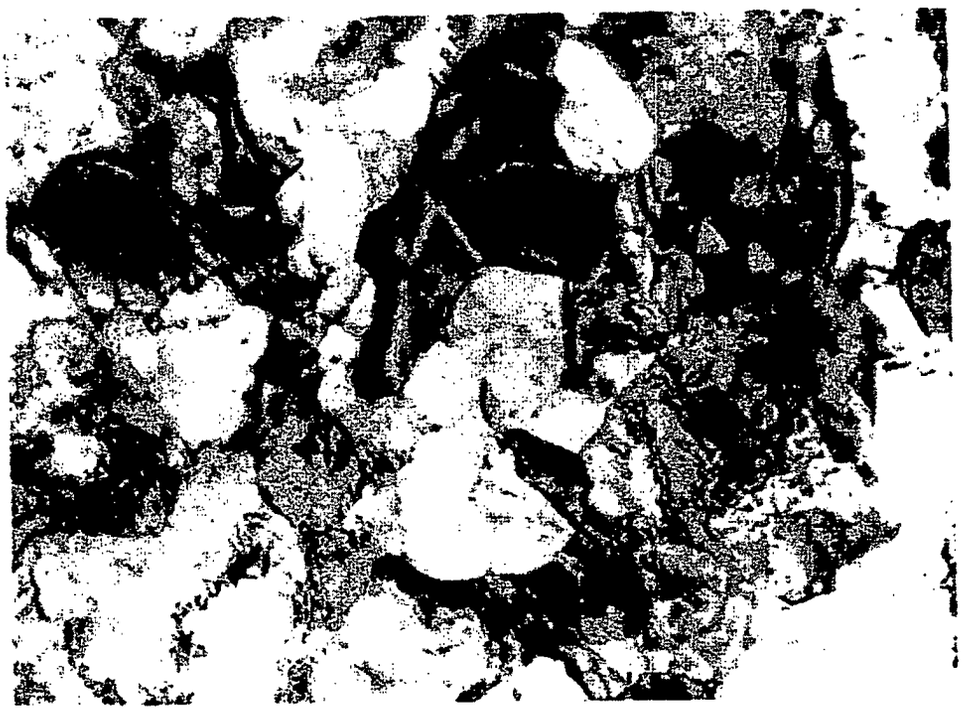
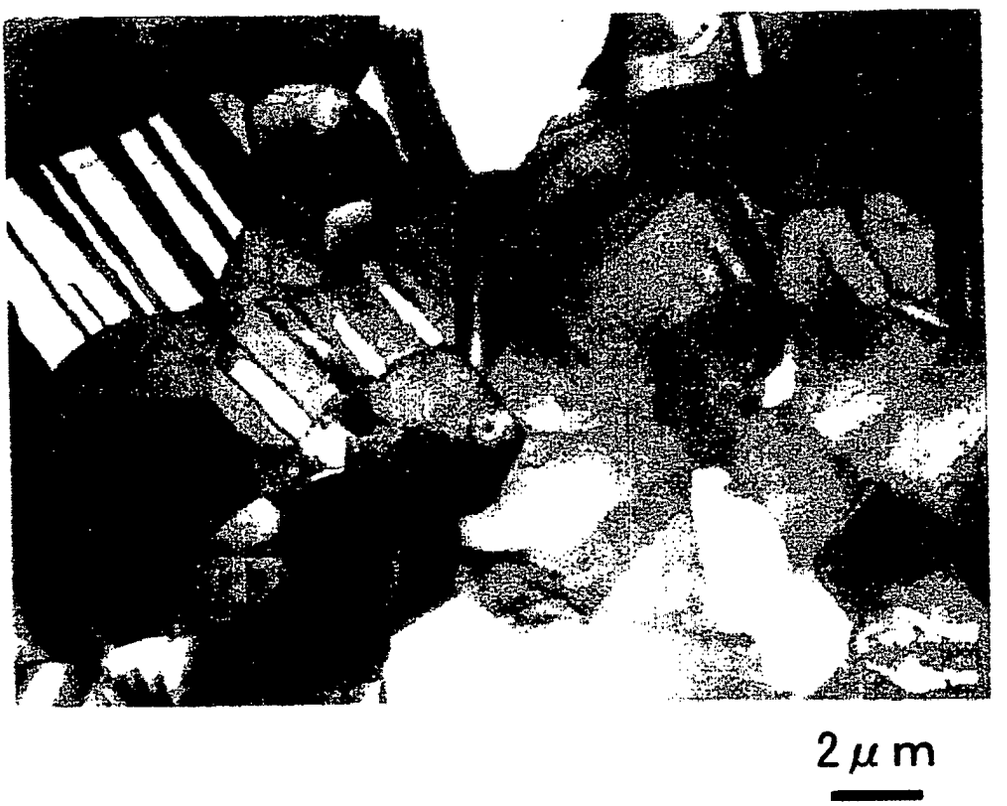

Small
Static recrystallization
Reduction
Dynamic recrystallization
Large
(Small misorientation)
Annealing
Generation and growth of recrystallized nuclei
Discontinuous recrystallization
(Large misorientation)
Annealing
Recovery
(grains with high boundary)
Continuous recrystallization

Fig. 2



Dynamic recrystallization (continuous recrystallization)

Fig. 3



Static recrystallization

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 00 6886

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	FERRASSE S ET AL: "MICROSTRUCTURE AND PROPERTIES OF COPPER AND ALUMINUM ALLOY 3003 HEAVILY WORKED BY EQUAL CHANNEL ANGULAR EXTRUSION" METALLURGICAL AND MATERIALS TRANSACTIONS A: PHYSICAL METALLURGY &MATERIALS SCIENCE, THE MINERALS, METALS AND MATERIALS SOCIETY, US, vol. 28A, no. 4, April 1997 (1997-04), pages 1047-1057, XP001002966 ISSN: 1073-5623 * page 1050 - page 1051; figures 3,5 *	1,2,5,7	C22F1/08 B21B3/00
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The present search report has been drawn up for all claims

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THE HAGUE	22 July 2002	Gregg, N

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