(11) EP 2 423 339 A1

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 153(4) EPC

(43) Date of publication:

29.02.2012 Bulletin 2012/09

(21) Application number: 10767017.6

(22) Date of filing: 16.04.2010

(51) Int Cl.:

C22C 9/04 (2006.01)

C22F 1/08 (2006.01)

C22F 1/00 (2006.01)

(86) International application number:

PCT/JP2010/056854

(87) International publication number:

WO 2010/122960 (28.10.2010 Gazette 2010/43)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: 24.04.2009 JP 2009106162

(71) Applicants:

 San-Etsu Metals Co., Ltd Takaoka-shi, Toyama 9330002 (JP)

 Kondoh, Katsuyoshi Osaka 562-0043 (JP)

(72) Inventors:

 KONDOH, Katsuyoshi Minoh-shi
 Osaka 562-0043 (JP) KOSAKA, Yoshiharu Tonami-shi Toyama 939-1315 (JP)

 KOJIMA, Akimichi Tonami-shi

Toyama 939-1315 (JP)

(74) Representative: Kirschner, Klaus Dieter et al

Puschmann Borchert Bardehle Patentanwälte Partnerschaft

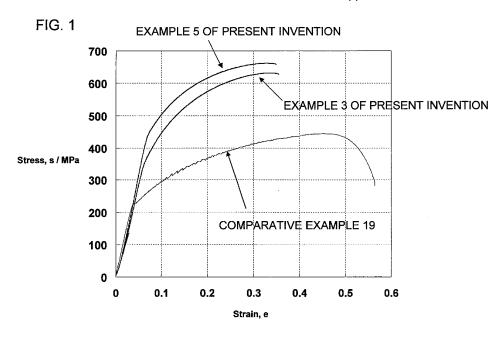
Bajuwarenring 21

82041 Oberhaching (DE)

(54) HIGH-STRENGTH COPPER ALLOY

(57) A high-strength copper alloy contains 20 to 45%

of zinc, 0.3 to 1.5% of iron, 0.3 to 1.5% of chromium, and a balance of copper, based on mass.



EP 2 423 339 A1

Description

Technical Field

[0001] The present invention relates to high-strength copper alloys having excellent mechanical characteristics, and more particularly to high-strength copper alloys produced by a casting method. More preferably, the present invention is intended to provide high-strength copper alloys having strength characteristics improved by performing hot plastic working on cast copper alloys.

10 Background Art

20

30

35

40

50

55

[0002] Copper alloys are widely used in automotive parts, parts of home electric appliances, electric, electronic, or optical parts, piping members (faucet fittings, valves), etc. In view of the recent measures against global warming, there has been a strong demand for reduction in size, weight, and thickness of products and members has been greatly desired, and the copper alloys having higher specific gravity than iron need to be increased in strength in order to meet such a demand.

[0003] Of the copper alloys, brass alloys containing zinc are often used in such parts as described above, due to their corrosion resistance. Japanese Unexamined Patent Publication No. 2000-119775 (Patent Literature 1) has been proposed as related art for increasing the strength of the brass alloys. Patent Literature 1 discloses that a brass alloy having tensile strength characteristics as high as about 600 to 800 MPa is obtained by hot extrusion of a cast copper alloy. Silicon (Si) as an added element has an advantage in that it forms γ -phase forming a matrix, and thus improves a cutting property of a copper alloy. However, since Si is hard, adding Si causes problems such as higher cutting resistance and a shorter tool life as compared to brass alloys as described in JIS H 3250-C3604, C3771, etc.

[0004] Other literatures disclosing high-strength copper alloys include Japanese Patent No. 3,917,304 (free-cutting copper alloy, Patent Literature 2) and Japanese Patent No. 3,734,372 (lead-free free-cutting copper alloy, Patent Literature 3). In the techniques disclosed in these patent literatures, it is proposed that a small amount of zirconium and phosphorus be added to obtain granular crystal rather than dendrite crystal formed by a normal casting method, and the granular crystal be refined to 10 μ m, thereby implementing high strength and high ductility. However, in the brass alloys disclosed in these patent literatures, a matrix is significantly harder than conventional brass alloys, thereby causing problems such as a degraded cutting property and a shorter tool life.

[0005] Meanwhile, in Japanese Patent No. 4,190,570 (lead-free free-cutting copper alloy extruded material, Patent Literature 4), the inventors succeeded in improving the cutting property of a brass powder alloy extruded material and also obtaining high tensile strength thereof by producing brass alloy powder and adding graphite particles to the brass alloy powder instead of lead by using a powder metallurgy process. In a manufacturing method of a copper alloy disclosed in Patent Literature 4, copper alloy powder having fine crystal grains is produced by using a rapid solidification method, and this powder is formed and solidified by hot extrusion, whereby a copper alloy base material having a fine structure can be obtained. Thus, a copper alloy extruded material having high strength and high ductility is obtained. However, as compared to a typical manufacturing process of a brass alloy, the copper alloy powder need be first formed and solidified in order to prepare a billet body for extrusion. It is therefore difficult to apply this manufacturing method to a conventional process of extruding a cast billet, and a press forming machine, a compacting apparatus, etc. is required to solidify the copper alloy powder.

Citation List

45 Patent Literature

[0006]

PTL1: Japanese Unexamined Patent Publication No. 2000-119775

PTL2: Japanese Patent No. 3,917,304 PTL3: Japanese Patent No. 3,734,372 PTL4: Japanese Patent No. 4,190,570

Summary of Invention

Technical Problem

[0007] It is an object of the present invention to manufacture a copper alloy having high strength characteristics by a

casting process. In order to achieve this object, the present invention proposes a copper-zinc alloy containing a proper amount of iron and chromium. Thus, the high-strength copper alloy according to the present invention is widely applicable to automotive parts, parts of home electric appliances, electric, electronic, or optical parts, piping members, etc.

5 Solution to Problem

[0008] A high-strength copper alloy according to the present invention contains 20 to 45% of zinc, 0.3 to 1.5% of iron, 0.3 to 1.5% of chromium, and a balance of copper, based on mass.

[0009] Preferably, in the high-strength copper alloy, a content ratio (Fe/Cr) of the iron to the chromium is 0.5 to 2 based on mass.

[0010] In one embodiment, the high-strength copper alloy further contains at least one kind of element selected from the group consisting of 0.05 to 4% of lead, 0.02 to 3.5% of bismuth, 0.02 to 0.4% of tellurium, 0.02 to 0.4% of selenium, and 0.02 to 0.15% of antimony, based on mass. The high-strength copper alloy may further contain 0.2 to 3.5% of aluminum and 0.3 to 3.5% of calcium, based on mass. The high-strength copper alloy may further contain at least one kind of element selected from a lanthanoid group consisting of lanthanum, cerium, neodymium, gadolinium, dysprosium, ytterbium, and samarium, and a total content of the at least one kind of element may be 0.5 to 5%, based on mass. The high-strength copper alloy may further contain at least one kind of element selected from the group consisting of 0.5 to 3% of manganese, 0.2 to 1% of silicon, 1.5 to 4% of nickel, 0.1 to 1.2% of titanium, 0.1 to 1.5% of cobalt, and 0.5 to 2.5% of zirconium, based on mass.

[0011] Preferably, the high-strength copper alloy includes iron-chromium compound particles at grain boundaries. The iron-chromium compound particles are particles precipitated at the grain boundaries during solidification in a casting method, and preferably have a particle size of 10 to 50 μ m.

[0012] Preferably, the copper alloy is a copper alloy subjected to hot plastic working after being produced by a casting method. The hot plastic working is, e.g., a working method selected from the group consisting of extrusion, forging, rolling, drawing, and pulling.

[0013] The configurations, functions, advantageous effects, etc. of the present invention described above will be described below in "Description of Embodiments."

Brief Description of Drawings

[0014]

20

30

35

45

50

55

[Fig. 1] Fig. 1 is a stress-strain diagram in a tension test.

[Fig. 2] Fig. 2 shows images showing a result of structure observation by an optical microscope.

[Fig. 3] Fig. 3 shows an image showing a result of SEM-EDS analysis of a brass alloy extruded material.

[Fig. 4] Fig. 4 is a diagram illustrating a hole drilling test method.

Description of Embodiments

40 [Addition of Iron and Chromium]

[0015] In a copper alloy of the present invention, iron and chromium are essential elements to be added. The iron content is 0.3 to 1.5%, and the chromium content is 0.3 to 1.5%, based on mass. Since chromium has low solid solubility in copper, a copper-chromium mother alloy is prepared, and is added to molten pure copper melted in a crucible, thereby adjusting the chromium content. Next, a predetermined weight of iron is added. Then, other element or elements are added as required, and lastly, zinc is added. The mixture is stirred and poured into a casting mold. Zinc tends to evaporate as compared to other elements due to its high vapor pressure. Thus, zinc is lastly added to the molten copper alloy.

[0016] The molten copper alloy is cooled and solidified in the casting mold. During the cooling and solidification, chromium slightly solid-solved in copper is crystallized at copper grain boundaries, and then iron is crystallized near the crystallized chromium. Thus, chromium-iron compound particles having a size (particle size) of about 10 to 50 μ m are present at the grain boundaries, and strength of the brass alloy is increased due to dispersion strengthening by the compound particles at the grain boundaries.

[0017] In Japanese Patent No. 4,190,570 (lead-free free-cutting copper alloy extruded material) as well, the inventors describe the effect of improving strength of the brass alloy by adding iron and chromium. However, the invention described in this patent is based on a powder metallurgy process by a rapid solidification method as a basic manufacturing method, chromium and iron, supersaturatedly solid-solved in copper alloy powder, are precipitated during an extrusion process, and are precipitated at grain boundaries or inside crystal grains as an iron-chromium compound as small as several hundreds of nanometers to several microns. Such submicron fine iron-chromium compound particles that are precipitated

based on the powder metallurgy process are completely different in a grain size and a production mechanism from the iron-chromium particles (compound particles) crystallized at the grain boundaries during solidification by a casting method as proposed in the present invention.

[0018] Regarding the iron content and the chromium content that are suitable for strengthening the brass alloy, it is desirable that the brass alloy contain 0.3 to 1.5% of iron and 0.3 to 1.5% of chromium, based on mass. The effect of improving the strength of the brass alloy as described above is not sufficient if the iron content and the chromium content are less than 0.3%. On the other hand, ductility of the brass alloy is reduced if the iron content and the chromium content are more than 1.5%. Corrosion resistance of the brass alloy is reduced if the iron content is more than 2%.

[0019] It is desirable that the content ratio (Fe/Cr) of iron to chromium be 0.5 to 2, based on mass. The proportion of the chromium-iron compound at the grain boundaries described above increases in the case where the content ratio of iron to chromium is in this range. In other words, if the content ratio of iron to chromium is less than 0.5 or more than 2, iron or chromium is independently crystallized at the grain boundaries, whereby the effect of improving the strength is reduced.

15 [Addition of Element for Improving Cutting Property]

[0020] In order to improve the cutting property of the brass alloy, it is desirable that the brass alloy contains at least one kind of element selected from the group consisting of 0.05 to 4% of lead, 0.02 to 3.5% of bismuth, 0.02 to 0.4% of tellurium, 0.02 to 0.4% of selenium, and 0.02 to 0.15% of antimony, based on mass. If the content of each element is less than the lower limit of the above range, a sufficient cutting property cannot be obtained, and a brass alloy base material has a rough surface after a cutting process, and the tool life is reduced. On the other hand, if the content of each element is more than the upper limit of the above range, mechanical characteristics such as strength and ductility are degraded because the element serves as an origin of fracture. Note that in view of the recent environmental problems, since the use of lead is restricted, it is more preferable to select bismuth as an element for improving the cutting property.

[Various Added Elements]

[0021] Tin is effective not only in forming γ -phase in the matrix, but also in increasing the strength of the alloy by forming a compound with copper. A preferred tin content is 0.2 to 3% based on mass. The effect described above is not sufficient if the tin content is less than 0.2%. On the other hand, adding more than 3% of tin reduces the ductility of the brass alloy. Adding more than 2% (the content) of tin improves dezincing resistance of β -phase.

[0022] Aluminum forms an intermetallic compound with copper, and its spherical particles are dispersed in the matrix, thereby improving mechanical characteristics such as strength and hardness, and high-temperature oxidation resistance of the copper alloy. A preferred aluminum content is 0.2 to 3.5% based on mass. The above effect of aluminum is not sufficient if the aluminum content is less than 0.2%. On the other hand, adding more than 3.5% of aluminum coarsens the compound with copper, resulting in reduced ductility of the brass alloy. Moreover, since aluminum, together with calcium described below, forms an intermetallic compound Al₂Ca, thereby contributing to improvement in strength and hardness.

[0023] Calcium, contained together with aluminum in the copper alloy, forms the intermetallic compound Al₂Ca, thereby contributing to improvement in strength and hardness. A preferred calcium content is 0.3 to 3.5% based on mass. The above effect is not sufficient if the calcium content is less than 0.3%. On the other hand, adding more than 3.5% of calcium coarsens the intermetallic compound Al₂Ca, resulting in reduced ductility of the brass alloy.

[0024] A lanthanoid group (lanthanum, cerium, neodymium, gadolinium, dysprosium, ytterbium, and samarium) is effective as each element of the lanthanoid group is precipitated at grain boundaries as a compound with copper or is independently crystallized at the grain boundaries, and thus strengthens the matrix. It is desirable that the total content of the lanthanoid element group be 0.5 to 5% based on mass. The effect of the lanthanoid element group is not sufficient if the total content thereof is less than 0.5%. Adding more than 5% of the lanthanoid element group reduces the ductility, and also excessively hardens the copper alloy, thereby reducing extrusion workability.

[0025] The strength and hardness of the copper alloy can be improved by adding at least one kind of element selected from the group consisting of 0.5 to 3% of manganese, 0.2 to 1% of silicon, 1.5 to 4% of nickel, 0.1 to 1.2% of titanium, 0.1 to 1.5% of cobalt, and 0.5 to 2.5% of zirconium as a transition metal element group, based on mass. The above effect of improving the characteristics is not sufficient if the content of each element is less than the lower limit of the above range. On the other hand, the ductility of the copper alloy is reduced if the content of each element exceeds the upper limit of the above range.

[Manufacturing Method]

[0026] A molten copper alloy having the above composition is produced, and an ingot material is produced by a method

4

55

20

25

30

35

40

45

in which the molten copper alloy is poured into a casting mold, or a continuous casting method. Moreover, hot plastic working, such as an extrusion, forging, rolling, drawing, or pulling, is performed on the ingot material as necessary. At this time, the heating temperature that allows the ingot to be sufficiently plastic-deformed is in the range of 600 to 850°C. In particular, the heating temperature is desirably 750°C or less in order to suppress evaporation of zinc during heating.

Examples

5

20

30

40

50

55

(1) Example 1

[0027] Cast copper alloy ingots containing elements shown in Tables 1 and 2 were prepared. Each ingot was subjected to a hot extrusion process immediately after heating and keeping the ingot at 700°C. The extrusion process was performed at an extrusion ratio of 37. Tensile test pieces were obtained from each copper alloy extruded material, and a tensile test was conducted at room temperature at a strain rate of 5×10^{-4} /s. The result is shown in Tables 1 and 2. Sample Nos. 1 to 16 are examples of the present invention, and Sample Nos. 17 to 19 are comparative examples.

[0028] [Table 1]

[0029] [Table 2]

[0030] Since Sample Nos. 1 to 5 as examples of the present invention contain a predetermined amount of iron and chromium, tensile strength (TS) of the extruded material is higher than Sample No. 19 as a comparative example by about 130 to 210 MPa. This is because iron-chromium compound particles made of iron and chromium are dispersed at grain boundaries, and thus the strength of the copper alloy is significantly increased. It is also recognized that the tensile strength is increased as the amount of iron and chromium is increased.

[0031] Sample Nos. 6 to 8 as examples of the present invention are copper alloys containing bismuth (Bi), and Sample Nos. 9 to 11 as examples of the present invention are copper alloys containing lead (Pb). Bismuth and lead are the elements that are added to improve the cutting property of the copper alloy. The tensile strength of the copper alloys of Sample Nos. 9 to 11 is slightly lower than Sample No. 2 as an example of the present invention containing neither bismuth nor lead, but is higher than Sample No. 17 or 18 as a comparative example by about 160 to 190 MPa. Thus, adding bismuth or lead to the brass alloy containing iron and chromium can improve the cutting property while maintaining high tensile strength.

[0032] In Sample Nos. 12 and 13 as examples of the present invention, it can be verified that the strength is increased by adding tin (Sn).

[0033] Sample Nos. 14 to 16 as examples of the present invention contain aluminum (A1) and calcium (Ca). Thus, the tensile strength is significantly increased by dispersion of an intermetallic compound Al₂Ca in the matrix of the copper alloy.

35 (2) Example 2

[0034] As in Example 1, cast copper alloy ingots containing elements shown in Tables 3 and 4 were prepared. Each ingot was subjected to a hot extrusion process immediately after heating and keeping the ingot at 700°C. The extrusion process was performed at an extrusion ratio of 37. Tensile test pieces were obtained from each copper alloy extruded material, and a tensile test was conducted at room temperature at a strain rate of 5×10^{-4} /s. The result is shown in Tables 3 and 4. Sample Nos. 20 to 24 and 28 to 33 are examples of the present invention, and Sample Nos. 25 to 27, 34, and 35 are comparative examples.

[0035] [Table 3]

[0036] [Table 4]

[0037] Each of Sample Nos. 21, 22, 23, and 24 as examples of the present invention contains a lanthanoid element. Thus, the tensile strength of these samples reaches 640 to 680 MPa, which is higher than Sample No. 20 as an example of the present invention containing no lanthanoid element. Each of Sample Nos. 29 and 30 as examples of the present invention is also a brass alloy containing a lanthanoid element. It can be verified that the tensile strength of these samples is significantly higher than Sample No. 28 as an example of the present invention containing no lanthanoid element.

[0038] Sample No. 31 as an example of the present invention is a brass alloy containing a proper amount of silicon (Si), Sample No. 32 as an example of the present invention is a brass alloy containing a proper amount of nickel (Ni), and Sample No. 33 as an example of the present invention is a brass alloy containing a proper amount of titanium (Ti). It can be verified that the tensile strength of these samples is higher than Sample No. 28 as an example of the present invention containing none of these elements.

[0039] Although Sample Nos. 25 to 27, 34, and 35 as comparative examples contain iron and chromium, the content ratio of iron to chromium is not in the range of 0.5 to 2, based on mass. Thus, it is recognized that the tensile strength of these samples is higher than Sample No. 19 as a comparative example containing neither iron nor chromium. However, the tensile strength of these elements is lower than the brass alloys as examples of the present invention whose content

ratio of iron to chromium is in the range of 0.5 to 2 (Sample Nos. 1 to 5 as examples of the present invention in Table 1, Sample No. 20 as an example of the present invention in Table 3, and Sample No. 28 as an example of the present invention in Table 4).

5 (3) Example 3

10

20

30

35

40

45

50

[0040] Tensile test pieces were obtained from the brass alloy extruded materials of Sample Nos. 3 and 5 as examples of the present invention and the brass extruded material of Sample No. 19 as a comparative example, and a tensile test was conducted. Fig. 1 shows a stress-strain diagram in this tensile test. It can be seen from the figure that Sample Nos. 3 and 5 as examples of the present invention have higher tensile strength and higher endurance strength (yield strength) than Sample No. 19 as a comparative example.

(4) Example 4

15 **[0041]** Fig. 2 shows the result of structure observation of Sample No. 3 as an example of the present invention by an optical microscope. It can be seen from the figure that Fe-Cr compound particles having a particle size of about 20 to 50 μm are uniformly dispersed in the brass alloy matrix.

(5) Example 5

[0042] Fig. 3 shows the result of scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis of the brass alloy extruded material of Sample No. 12 as an example of the present invention described in Example 1. It can be seen from the figure that main components of the compound that is dispersed are iron (Fe) and chromium (Cr).

25 (6) Example 6

[0043] Cast copper alloy ingots containing elements shown in Tables 5 and 6 are prepared. Tensile test pieces were obtained from each copper alloy ingot, and a tensile test was conducted at room temperature at a strain rate of 5×10^{-4} /s. The result is shown in Tables 5 and 6. Sample Nos. 1 to 16 are examples of the present invention, and Sample Nos. 17 to 19 are comparative examples. It can be seen that the strength of the examples of the present invention is higher than the comparative examples even in the cast ingot materials before the protrusion process, because the examples of the present invention contains a proper amount of predetermined elements.

[0044] [Table 5] [0045] [Table 6]

(7) Example 7

[0046] The cutting property of the brass alloy extruded materials of Sample Nos. 5 to 11 as examples of the present invention and Sample Nos. 17 to 19 as comparative examples described in Examples 1 and 2 were evaluated by conducting a drilling test. Note that as a test method, the time it takes to drill a hole having a depth of 5 mm in each copper alloy extruded material with constant load (in this example, with a weight of 1 kg) applied to a drill as shown in Fig. 4 was compared. Shorter processing time means a more satisfactory cutting property. Note that the drilling test was conducted for 10 samples per extruded material by rotating a high-speed steel drill having a diameter of 4.8 mm ϕ at a rotational speed of 1,000 rpm under dry conditions (with no cutting oil), and a mean value was obtained from the measurement values. The result is shown in Table 7.

[0047] [Table 7]

[0048] As shown in Table 7, in Sample No. 5 as an example of the present invention containing none of the elements that improve the cutting property such as bismuth and lead, a hole having a depth of 5 mm was not able to be formed under the above conditions even if the drilling was performed for three minutes. Sample Nos. 6 to 8 as examples of the present invention are brass alloys containing bismuth. In Sample Nos. 6 to 8, a hole was able to be formed, and the processing time decreases as the amount of bismuth is increased. Sample Nos. 9 to 11 as examples of the present invention are alloys containing lead, and the cutting time decreases as the lead content is increased. Thus, it was verified that adding bismuth or lead can significantly improve the cutting property while maintaining high tensile strength.

55 (8) Example 8

[0049] Cast copper alloy ingots containing elements shown in Table 8 were prepared. Each ingot was subjected to a hot extrusion process immediately after heating and keeping the ingot at 650°C. The extrusion process was performed

at an extrusion ratio of 37. Tensile test pieces were obtained from each copper alloy extruded material, and a tensile test was conducted at room temperature at a strain rate of 5×10^{-4} /s. Regarding evaluation of the cutting property, mean processing time was calculated by a method similar to that of Example 7 described above. The result is shown in Table 8. All of Sample Nos. 40 to 56 are examples of the present invention.

[0050] [Table 8]

[0051] As can be seen from Table 8, copper alloys having high tensile strength, high elongation (ductility), and a high cutting property can be obtained by adding to brass a proper amount of element that improves the strength and a proper amount of element that improves the cutting property.

10 (9) Example 9

15

20

35

40

45

50

55

[0052] Molten copper alloys containing elements shown in Table 9 were prepared, and powders having a powder particle size of 150 μ m or less (a mean particle size of 112 to 138 μ m) were produced by a water atomizing method. Each powder was heated and pressed (with a pressure of 40 MPa) in a vacuum atmosphere at 750°C by a discharge plasma sintering apparatus to produce a dense sintered compact. Each sintered compact was subjected to a hot extrusion process immediately after heating and keeping (for 15 minutes) the sintered compact at 650°C in a nitrogen gas atmosphere. The extrusion process was performed at an extrusion ratio of 37. Tensile test pieces were obtained from each copper alloy extruded material, and a tensile test was conducted at room temperature at a strain rate of 5 \times 10⁻⁴/s. Regarding evaluation of the cutting property, mean processing time was calculated by a method similar to that of Example 7 described above. The result is shown in Table 9. All of Sample Nos. 60 to 69 are examples of the present invention. [0053] [Table 9]

[0054] As can be seen from Table 9, copper alloys having high tensile strength, high elongation (ductility), and a high cutting property can be obtained by adding to brass a proper amount of element that improves the strength and a proper amount of element that improves the cutting property. In particular, in the case of using powder produced by the water atomizing method, a grain refining effect is additionally provided, and thus the tensile strength of the extruded material is further increased as compared to the case of producing the extrusion ingot by the casting method.

Industrial Applicability

[0055] The present invention can be advantageously used as a high-strength copper alloy having excellent mechanical characteristics.

					Table	e 1					
Sample No.	1	2	3	4	5	6	7	8	9	10	11
Zn	39.8	40.2	40.4	39.9	40.0	40.1	39.8	40.0	39.8	40.1	39.9
Fe	0.42	0.63	0.98	1.23	1.41	0.68	0.73	0.70	1.05	1.09	1.06
Cr	0.38	0.58	1.02	1.17	1.38	0.73	0.90	0.97	0.98	1.12	1.19
Sn	0.02	-	0.03	-	0.02	0.04	-	-	0.01	-	0.02
Bi	-	-	-	-	-	0.57	1.28	2.28	-	-	-
Pb	0.03	0.02	0.01	0.02	0.03	0.02	0.01	0.02	0.45	0.92	2.08
Al	-	-	-	-	-	-	-	-	-	-	-
Ca	-	-	-	-	-	-	-	-	-	-	-
Cu	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Fe/Cr Ratio	1.11	1.09	0.96	1.05	1.02	0.93	0.81	0.72	1.07	0.97	0.89
TS	587	609	624	647	665	598	589	580	609	600	587
ε	30.2	29.1	27.9	26.4	25.2	31.2	29.3	27.8	28.7	27.4	26.1
TS:Tensile St	trenath (MP	a) s ·Breaki	na Flonasti	on (%)		•	•			•	

TS;Tensile Strength (MPa), ϵ ;Breaking Elongation (%)

Table 2

17 Sample No. 12 13 14 15 16 18 19 40.2 40.7 39.7 39.4 39.2 40.1 39.8 40.4 Zn 5 Fe 0.72 0.69 0.82 0.99 0.87 0.02 0.03 0.01 Cr 0.97 0.87 0.98 1.19 1.03 ---Sn 0.98 2.13 ---10 -----2.27 --Bi 2.78 Pb 0.01 0.02 0.02 0.03 0.02 0.02 0.02 0.43 Αl --0.64 88.0 --Ca 0.37 0.55 0.69 15 Balance Cu Balance Balance Balance Balance Balance Balance Balance Fe/Cr Ratio 0.74 0.79 0.84 0.83 0.84 _ _ TS 644 662 644 658 668 402 411 453

26.2

TS;Tensile Strength (MPa), ϵ ;Breaking Elongation (%)

25.1

Tal

26.3

Table 3

25.3

24.4

39.8

38.7

48.9

Sample No.	20	21	22	23	24	25	26	27
Zn	40.1	40.4	39.8	39.3	40.2	40.2	40.0	40.3
Fe	0.97	0.89	0.88	0.93	0.90	0.84	0.86	0.92
Cr	0.89	0.83	0.88	0.86	0.83	0.23	0.31	0.33
Sn	0.01	0.02	0.03	0.02	0.03	0.03	0.01	0.02
Pb	0.03	0.02	0.01	0.02	0.03	0.02	0.01	0.02
La	-	1.09	2.54	-	-	-	-	-
Ce	ı	1	-	0.78	1	1	-	-
Nd	-	-	-	-	0.65	-	-	-
Gd	-	-	-	-	-	-	-	-
Yb	ı	1	-	1	1	1	-	-
Si	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-
Ti	1	1	-	1	1	1	-	-
Cu	Balance							
Fe/Cr Ratio	1.09	1.07	1.00	1.08	1.08	3.65	2.77	2.79
TS	618	641	683	662	652	554	563	567
ε	28.2	25.7	21.2	23.3	24.8	33.6	32.1	32.6

55

20

25

30

35

40

45

Table 4

Sample No.	28	29	30	31	32	33	34	35
Zn	39.4	40.3	39.6	40.1	40.4	39.5	39.3	40.4
Fe	0.62	0.58	0.59	0.62	0.60	0.64	0.57	0.60
Cr	0.60	0.59	0.62	0.61	0.62	0.65	0.21	0.17
Sn	0.01	-	0.02	0.02	0.03	-	0.02	-
Pb	0.45	0.92	2.08	0.01	0.02	0.02	0.03	0.02
La	-	-	-	-	-	-	-	-
Ce	-	-	-	-	-	-	-	-
Nd	-	-	-	-	-	-	-	-
Gd	-	1.65	-	-	-	-	-	-
Yb	-	-	1.32	-	-	-	-	-
Si	-	-	-	0.38	-	-	-	-
Ni	-	-	-	-	1.87	-	-	-
Ti	-	-	-	-	-	0.44	-	-
Cu	Balance							
Fe/Cr Ratio	1.03	0.98	0.95	1.02	0.97	0.98	2.71	3.53
TS	601	653	646	634	639	633	549	555
е	29.6	25.3	26.1	26.2	27.4	28.1	34.4	34.1

Table 5

					Tubic	, 0					
Sample No.	1	2	3	4	5	6	7	8	9	10	11
Zn	39.8	40.2	40.4	39.9	40.0	40.1	39.8	40.0	39.8	40.1	39.9
Fe	0.42	0.63	0.98	1.23	1.41	0.68	0.73	0.70	1.05	1.09	1.06
Cr	0.38	0.58	1.02	1.17	1.38	0.73	0.90	0.97	0.98	1.12	1.19
Sn	0.02	-	0.03	-	0.02	0.04	-	-	0.01	-	0.02
Bi	-	-	-	-	-	0.57	1.26	2.28	-	-	-
Pb	0.03	0.02	0.01	0.02	0.03	0.02	0.01	0.02	0.45	0.92	2.08
Al	-	-	-	-	-	-	-	-	-	-	-
Ca	-	-	-	-	-	-	-	-	-	-	-
Cu	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Fe/Cr Ratio	1.11	1.09	0.96	1.05	1.02	0.93	0.81	0.72	1.07	0.97	0.89
TS	442	449	464	477	482	437	441	422	449	452	426
ε	36.2	32.3	29.7	28.9	28.1	33.7	32.1	29.8	30.3	30.1	29.4
TS:Tensile St	renath (MP	a) c · Broak	ing Flongati	on (%)							

TS;Tensile Strength (MPa). ϵ ; Breaking Elongation (%)

Table 6

Sample No.	12	13	14	15	16	17	18	19
Zn	40.2	40.7	39.7	39.4	39.2	40.1	39.8	40.4
Fe	0.72	0.69	0.82	0.99	0.87	0.02	0.03	0.01
Cr	0.97	0.87	0.98	1.19	1.03	-	-	-
Sn	0.98	2.13	-	-	-	-	-	-
Bi	-	-	-	-	-	2.27	-	-
Pb	0.01	0.02	0.02	0.03	0.02	0.02	2.78	0.02
Al	-	-	0.43	0.64	0.88	-	-	-
Ca	-	-	0.37	0.55	0.69	-	-	-
Cu	Balance							
Fe/Cr Ratio	0.74	0.79	0.84	0.83	0.84	-	-	-
TS	473	481	467	482	485	301	308	332
ε	28.9	27.9	28.5	27.5	26.2	42.5	44.2	51.4

TS;Tensile Strength (MPa), ϵ ;Breaking Elongation (%)

Table 7

Sample No.	5	6	7	8	9	10	11	17	18	19
Mean Cutting Time	Unable to Cut	36.85	29.94	24.24	36.61	28.62	21.79	22.6	18.83	45.26
n=1	>180	38.7	31.1	24.4	33.2	29.2	21.2	22.4	19.2	38.2
n=2	>180	34.5	29.8	24.6	36.4	28.4	22.3	23.1	18.7	39.2
n=3	>180	36.6	30.2	24.3	38.3	28.1	21.8	23.7	18.3	40.2
n=4	>180	35.7	30.8	23.3	37.2	29.6	21.7	22.2	18.9	41.0
n=5	>180	37.2	28.8	24.1	34.3	28.4	21.5	22.6	19.0	42.0
n=6	>180	36.8	29.7	24.7	37.9	29.4	21.9	22.8	19.1	43.4
n=7	>180	36.6	29.2	25.1	38.2	28.3	22.1	22.3	18.7	46.6
n=8	>180	37.5	28.6	23.8	36.8	27.9	22.3	21.8	18.6	48.4
n=9	>180	37.7	30.4	23.9	37.6	28.8	21.7	22.5	19.1	54.4
n=10	>180	37.2	30.8	24.2	36.2	28.1	21.4	22.6	18.7	59.2
Drilling Load: :1kg	f, Drill Diameter;	5mm∅,	Hole Der	oth ; 5mm						

 5
 5

 5
 45

 40
 35

 30
 25

 20
 15

 10
 5

 55
 5

Table 8

			Added	Element	t(wt%)				Tensile Strength	Endurance Stress	Breaking Elongation	
Sample No.	Zn	Fe	Cr	Sn	Ti	Bi	Pb	Fe/Cr	MPa	MPa	%	Mean Cutting Time s
40	40.57	0.54	0.70	0.65		2.37		0.77	610.2	311.6	31.3	33.21
41	40.81	0.23	0.26	0.60		0.99		0.89	596.7	290.7	29.4	36.12
42	40.64	0.23	0.26	0.60		2.02		0.88	595.8	293.4	27.4	14.77
43	40.83	0.22	0.22	0.58		2.85		1.00	622.4	284.1	22.2	18.10
44	40.30	0.61	0.88	0.66		1.90		0.69	606.2	298.2	28.1	28.06
45	39.22	0.47	0.45	0.62		1.89		1.04	523.1	302.3	32.2	27.45
46	39.26	0.40	0.58	0.62		2.12		0.69	506.5	282.9	29.4	31.50
47	37.30	0.68	0.83	0.79			2.55	0.82	547.2	339.9	16.4	29.18
48	37.30	0.68	0.83	0.79			2.98	0.82	600.1	348.9	28.8	43.04
49	39.65	0.65	0.98	0.63			1.51	0.66	629.7	294.8	29.3	25.13
50	40.50	0.63	0.98	0.65			2.19	0.64	624.4	334.8	31.8	33.08
51	40.31	0.51	0.73	0.66			2.45	0.70	600.8	291.0	34.8	26.89
52	40.44	0.33	0.49	0.64			2.28	0.67	613.7	322.9	33.6	35.73
53	40.86	0.22	0.34	0.59			2.97	0.65	582.1	284.8	36.8	22.37
54	40.03	0.43	0.54	0.98			2.03	0.80	629.7	294.8	28.5	35.08
55	39.81	0.38	0.67	0.65	0.99		2.95	0.57	604.6	222.3	34.4	29.52
56	39.43	0.31	0.37	0.64	0.89		3.24	0.84	550.4	245.0	36.8	20.82

50 45 40 35 30 25

Table 9

15

10

5

			۸ ما ما م ما		L/+0/ \							
			Added	Element	t(Wt%)			Fe/Cr	Tensile Strength	Endurance Stress	Breaking Elongation	Mean Cutting Time s
Sample No.	Zn	Fe	Cr	Sn	Ti	Bi	Pb	1 0/01	MPa	MPa	%	Wearr outling Time 3
60	40.57	0.54	0.70	0.65		1.01	1.23	0.77	605.6	379.9	16.2	33.45
61	40.30	0.61	0.88	0.66		1.90	1.32	0.69	586.5	363.4	12.9	32.05
62	40.30	0.61	0.88	0.66		1.90	1.28	0.69	586.6	378.4	9.7	36.07
63	40.50	0.63	0.98	0.65			2.98	0.64	626.7	364.4	25.2	24.56
64	40.50	0.63	0.98	0.65			2.65	0.64	646.2	393.2	19.1	29.61
65	40.31	0.51	0.73	0.66			3.13	0.70	604.1	365.0	23.6	22.17
66	40.86	0.22	0.34	0.59			3.53	0.65	580.0	332.0	33.6	19.25
67	40.03	0.43	0.54	0.98			2.45	0.80	626.4	324.4	25.7	28.29
68	40.03	0.43	0.54	0.98			2.34	0.80	646.2	389.9	19.1	31.87
69	39.81	0.30	0.56	0.65	0.99		2.54	0.54	654.3	457.1	19.3	27.25

Claims

5

10

15

40

55

- **1.** A high-strength copper alloy containing 20 to 45% of zinc, 0.3 to 1.5% of iron, 0.3 to 1.5% of chromium, and a balance of copper, based on mass.
- 2. The high-strength copper alloy according to claim 1, wherein a content ratio (Fe/Cr) of said iron to said chromium is 0.5 to 2 based on mass.
- 3. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from the group consisting of 0.05 to 4% of lead, 0.02 to 3.5% of bismuth, 0.02 to 0.4% of tellurium, 0.02 to 0.4% of selenium, and 0.02 to 0.15% of antimony, based on mass.
- **4.** The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains 0.2 to 3% of tin, based on mass.
- 5. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains 0.2 to 3.5% of aluminum and 0.3 to 3.5% of calcium, based on mass.
- 20 6. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from a lanthanoid group consisting of lanthanum, cerium, neodymium, gadolinium, dysprosium, ytterbium, and samarium, and a total content of said at least one kind of element is 0.5 to 5%, based on mass.
- 7. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from the group consisting of 0.5 to 3% of manganese, 0.2 to 1% of silicon, 1.5 to 4% of nickel, 0.1 to 1.2% of titanium, 0.1 to 1.5% of cobalt, and 0.5 to 2.5% of zirconium, based on mass.
- **8.** The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy includes iron-chromium compound particles at grain boundaries.
 - **9.** The high-strength copper alloy according to claim 8, wherein said iron-chromium compound particles are particles precipitated at said grain boundaries during solidification in a casting method.
- 10. The high-strength copper alloy according to claim 9, wherein said iron-chromium compound particles have a particle size of 10 to 50 μm.
 - **11.** The high-strength copper alloy according to claim 1, wherein said copper alloy is a copper alloy subjected to hot plastic working after being produced by a casting method.
 - **12.** The high-strength copper alloy according to claim 11, wherein said hot plastic working is a working method selected from the group consisting of extrusion, forging, rolling, drawing, and pulsing.

45 Amended claims under Art. 19.1 PCT

- **1.** Amended) A high-strength copper alloy containing 20 to 45% of zinc, 0.3 to 1.5% of iron, 0.3 to 1.5% of chromium, 0.2 to 3.5% of aluminum, 0.3 to 3.5% of calcium, and a balance of copper, based on mass.
- **2.** The high-strength copper alloy according to claim 1, wherein a content ratio (Fe/Cr) of said iron to said chromium is 0.5 to 2 based on mass.
 - 3. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from the group consisting of 0.05 to 4% of lead, 0.02 to 3.5% of bismuth, 0.02 to 0.4% of tellurium, 0.02 to 0.4% of selenium, and 0.02 to 0.15% of antimony, based on mass.
 - 4. The high-strength copper alloy according to claim 1, wherein

said high-strength copper alloy further contains 0.2 to 3% of tin, based on mass.

5. Deleted.

20

30

40

45

50

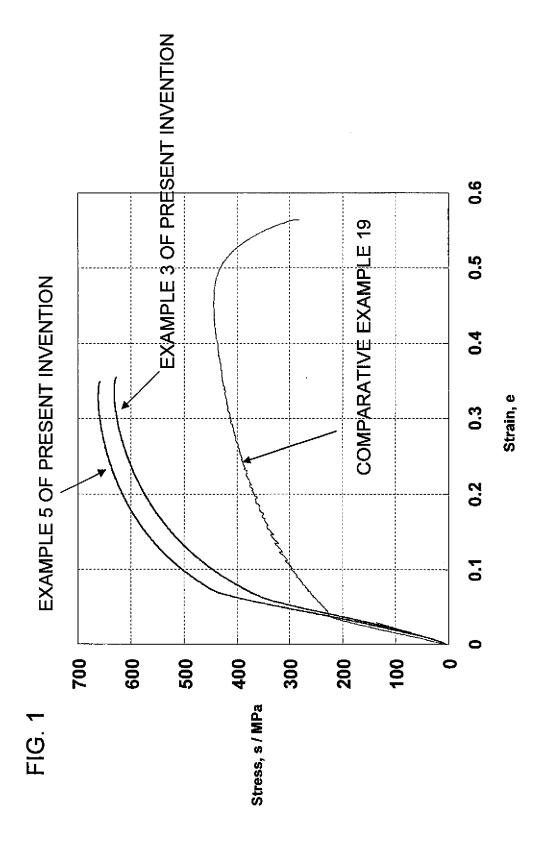
55

- 6. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from a lanthanoid group consisting of lanthanum, cerium, neodymium, gadolinium, dysprosium, ytterbium, and samarium, and a total content of said at least one kind of element is 0.5 to 5%, based on mass.
- 7. The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy further contains at least one kind of element selected from the group consisting of 0.5 to 3% of manganese, 0.2 to 1% of silicon, 1.5 to 4% of nickel, 0.1 to 1.2% of titanium, 0.1 to 1.5% of cobalt, and 0.5 to 2.5% of zirconium, based on mass.
- **8.** The high-strength copper alloy according to claim 1, wherein said high-strength copper alloy includes iron-chromium compound particles at grain boundaries.
 - **9.** The high-strength copper alloy according to claim 8, wherein said iron-chromium compound particles are particles precipitated at said grain boundaries during solidification in a casting method.
 - **10.** The high-strength copper alloy according to claim 9, wherein said iron-chromium compound particles have a particle size of 10 to 50 μ m.
- 25 11. The high-strength copper alloy according to claim 1, wherein said copper alloy is a copper alloy subjected to hot plastic working after being produced by a casting method.
 - **12.** The high-strength copper alloy according to claim 11, wherein said hot plastic working is a working method selected from the group consisting of extrusion, forging, rolling, drawing, and pulling.

Statement under Art. 19.1 PCT

In the written opinion of the International Searching Authority about the present application, it was recognized that the invention according to originally filed claims 5 and 6 is novel and non-obvious. Therefore, the claims have been amended as follows.

The limitation of originally filed claim 5 is included in claim 1. Originally filed claim 5 is deleted.



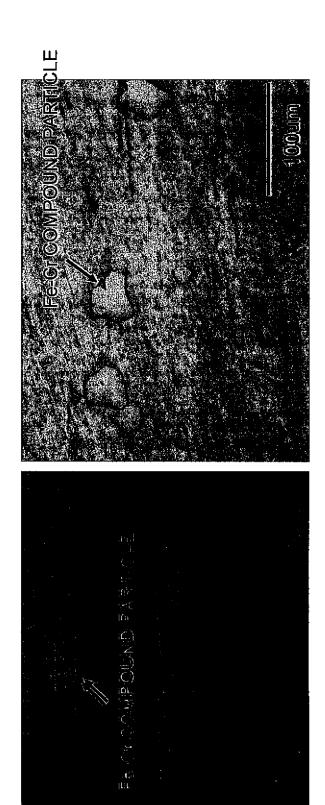
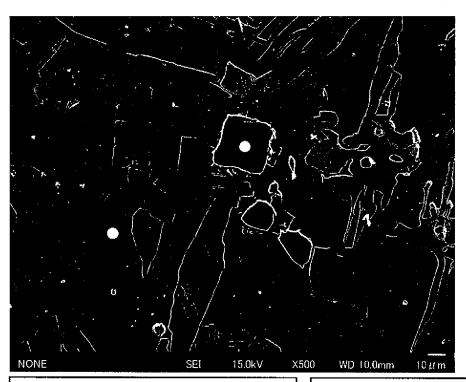
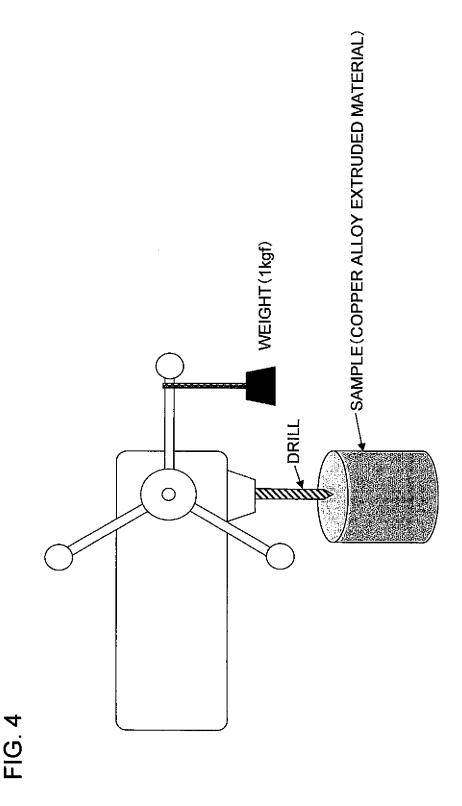


FIG. 3



Point 1	(COMPOU	ND PART	ICLE)
	(keV)	wt%	at%
СК	0.277	2.3	9.1
ОК	0.525	1.97	5.99
Cr K	5.411	62.88	57.8
Fe K	6.398	25.92	22.2
Cu K	8.04	0.89	0.7
Zn K	8.63	5.67	4.2
Sn L	-	-	-
Ві М	2.419	0.36	0.09
To	otal	100	100

Point 2	(MATRIX)		
	(keV)	wt%	at%
СК	0.277	3.57	16.0
ОК	0.525	1.36	4.6
Cr K	5.411	0.09	0.1
Fe K	6.398	0.57	0.6
Cu K	8.04	51.65	43.9
Zn K	8.63	41.39	34.2
Sn L	3.442	1.28	0.6
Ві М	2.419	0.09	0.02
То	tal	100	100



INTERNATIONAL SEARCH REPORT

International application No.

		PCT/JPZ	010/056854
	CATION OF SUBJECT MATTER 2006.01)i, C22F1/08(2006.01)i,	C22F1/00(2006.01)n	
According to Inte	ernational Patent Classification (IPC) or to both national	l classification and IPC	
B. FIELDS SE	ARCHED		
	nentation searched (classification system followed by cla C22F1/08, C22F1/00	assification symbols)	
Jitsuyo Kokai Ji	itsuyo Shinan Koho 1971-2010 To	tsuyo Shinan Toroku Koho roku Jitsuyo Shinan Koho	1996-2010 1994-2010
Electronic data b	ase consulted during the international search (name of d	lata base and, where practicable, search ter	ms used)
C. DOCUMEN	VTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.
X A	JP 2008-1964 A (Chuetsu Metal Ltd.), 10 January 2008 (10.01.2008), claim 1; paragraphs [0009], [fig. 1 (Family: none)	·	1-4,7-12 5,6
Х	JP 3-36227 A (Mitsubishi Meta 15 February 1991 (15.02.1991) claim 3; table 1-2 (Family: none)		7
А	JP 3-47932 A (Mitsubishi Meta 28 February 1991 (28.02.1991) claim 3 (Family: none)		7
× Further do	ocuments are listed in the continuation of Box C.	See patent family annex.	
"A" document d to be of part	gories of cited documents: efining the general state of the art which is not considered icular relevance	"T" later document published after the inte date and not in conflict with the applica the principle or theory underlying the in	tion but cited to understand
filing date	cation or patent but published on or after the international which may throw doubts on priority claim(s) or which is	"X" document of particular relevance; the considered novel or cannot be considered when the document is taken alone	
"O" document per the priority of	ablish the publication date of another citation or other on (as specified) eferring to an oral disclosure, use, exhibition or other means ublished prior to the international filing date but later than date claimed	"Y" document of particular relevance; the cl considered to involve an inventive s combined with one or more other such being obvious to a person skilled in the "&" document member of the same patent for	step when the document is documents, such combination art amily
05 July	al completion of the international search y, 2010 (05.07.10)	Date of mailing of the international search 20 July, 2010 (20.0	
	ng address of the ISA/ se Patent Office	Authorized officer	

Facsimile No.
Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/056854

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
А	JP 7-310133 A (Chuetsu Metal Works Co., Ltd.), 28 November 1995 (28.11.1995), claim 3; paragraphs [0001], [0025], [0029] (Family: none)	1-12
A	JP 5-230567 A (Mitsubishi Materials Corp.), 07 September 1993 (07.09.1993), claims 3, 4; paragraphs [0014] to [0027] (Family: none)	1-12
A	JP 2008-208466 A (Dowa Metaltech Co., Ltd.), 11 September 2008 (11.09.2008), claims (Family: none)	1-12
А	JP 2004-285449 A (Dowa Mining Co., Ltd.), 14 October 2004 (14.10.2004), claims; paragraphs [0033] to [0049] (Family: none)	1-12
A	JP 9-316570 A (Chuetsu Metal Works Co., Ltd.), 09 December 1997 (09.12.1997), claims 2, 4; paragraphs [0022] to [0032] (Family: none)	1-12
A	JP 60-86233 A (Nippon Mining Co., Ltd.), 15 May 1985 (15.05.1985), claims; page 2, lower left column, lines 11 to 20 (Family: none)	1-12

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2000119775 A [0003] [0006]
- JP 3917304 B [0004] [0006]

- JP 3734372 B [0004] [0006]
- JP 4190570 B [0005] [0006] [0017]