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(54) COLD- AND HOT-WATER PIPING MADE OF PITTING-RESISTANT COPPER ALLOY.

(57) A cold- and hot-water piping made of a pitting-resistant copper alloy which contains niobium and/or tantalum in a total amount of 0.005-5 wt. %, further contains, if necessary, at least one element selected from among: (i) yttrium and/or zirconium in a total amount of 0.005-1 wt. %, (ii) tin and/or silver in a total amount of 0.05-5 wt. %, (iii) at least one element selected from the group consisting of titanium and R (rare earth elements other than yttrium) in a total amount of 0.005-1 wt. %, and (iv) tungsten in an amount of 0.003-0.5 wt. %, and still further contains, if necessary, phosphorus in an amount of 0.005-0.5 wt. %.

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FIELD OF TECHNOLOGY

The present invention relates to a copper alloy piping for supplying cold and hot water which piping has an excellent pitting corrosion resistance.

TECHNICAL BACKGROUND

Pipings of copper obtained by deoxidizing the molten electrolytic copper with phosphorus have been widely used as pitting corrosion resistant pipings for supplying cold and hot water in hotels, hospitals and apartment houses. This is because the pipings of copper deoxidized with phosphorus are excellent in corrosion resistance, workability, operability, etc. and thus are used very suitably as pitting corrosion resistant pipings for supplying cold and hot water.

However, even when the pipings of copper deoxidized with phosphorus are used, leakage accidents have occurred, though rarely, due to the pitting corrosion, causing a problem. Pitting corrosion is roughly divided into two types: Type I and Type II. The pitting corrosion of Type I is caused by cold hard water mainly in Europe. In Japan, pitting corrosion of Type II occurs due to the hot soft water.

Pitting corrosion of Type II occurs as follows. When the anion ratio in water $[SO_4^{2-}]/[HCO_3^-]$ is greater than 1 and the residual chlorine concentration is high, ClO_2^- concentrates below a Cu_2O layer formed on the inner surface of the copper alloy piping and acts as a strong oxidizing agent. The ClO_2^- is reduced to bring about a cathodic reaction and oxidizes Cu to form CuO. Simultaneously, the ClO_2^- produces the corrosive anion Cl^-, which serves as a starting point of pitting corrosion. The Cl^- concentrates over the time. The H^+ concentrates as Cl^- concentrates, thereby causing the reduction in pH. In this way, the pitting corrosion of Type II progresses.

There have been proposed a variety of copper alloy pipings resistant to pitting corrosion of Type II. For example, Japanese Examined Patent Publication No. 62-34821 discloses a pitting corrosion resistant copper alloy piping for supplying cold and hot water, the copper alloy containing 0.01 to 1 weight % of Al, 0.03 to 2.5 weight % of Sn [where $(Al + Sn) \geqq 0.1$ weight %], 0.005 to 0.5 weight % of one or more of P, Mg, B, Mn, and Si, not more than 100 ppm of O, remainder Cu and unavoidable impurities.

DISCLOSURE OF THE INVENTION

However, the Cu-Al-Sn copper alloy piping disclosed in the above publication has the problem of poor brasing ability, weldability and workability because of its content of Al. Further, due to the recent increase of SO_4^{2-} resulting from the acid rain, increase of the residual chlorine concentration resulting from the strengthening of the chlorine sterilization caused by the deteriorated quality of water, and increase of the sulphate ion resulting from an increased addition of aluminum alum as a coprecipitating agent, the anion ratio $[SO_4^{2-}]/[HCO_3^-]$ in water has become far greater than 1 and the residual chlorine concentration has become higher. Thus, the pitting corrosion of Type II is now more liable to occur than before. The conventional copper alloy pipings are not very satisfactory in responding to this situation and there has been a strong demand for the development of a copper alloy piping having an excellent pitting corrosion resistance.

In order to meet the above demand, the inventors of the present invention carried out a research to develop a copper alloy piping having a better pitting corrosion resistance than the conventional copper alloy pipings and obtained the following results.

(a) The piping of the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta has a better pitting corrosion resistance than the conventional copper alloy pipings because the occurrence and progress of the pitting corrosion are suppressed. This piping demonstrates a practically very satisfactory effect when being used as a pitting corrosion resistant copper alloy piping for supplying hot and cold water.

(b) When a total amount of 0.005 to 1 weight % of Y and/or Zr are added further to the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta, the pitting corrosion resistance is further improved.

(c) When a total amount of 0.05 to 5 weight % of Sn and/or Ag are added further to the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta, the pitting corrosion resistance is further improved.

(d) When a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R (where R denotes rare earth elements except Y) are added further to the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta, the pitting corrosion resistance is further improved.

(e) When 0.003 to 0.5 weight % of W is added further to the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta, the pitting corrosion resistance is further improved.
(f) When one or more of the following (i), (ii), (iii) and (iv):
(i) a total amount of 0.005 to 1 weight % of Y and/or Zr,
(ii) a total amount of 0.05 to 5 weight % of Sn and/or Ag,
(iii) a total amount of 0.005 to 1 weight % of Ti and R,
(iv) 0.003 to 0.5 weight % of W,
are added further to the copper alloy containing a total amount of 0.005 to 5 weight % of Nb and/or Ta, the pitting corrosion resistance is further improved.
(g) When 0.005 to 0.5 weight % of P is added further to the copper alloy (a) to (f) whose pitting corrosion resistance is improved, the pitting corrosion resistance is furthermore improved.

The invention was developed on the basis of these research results and is directed to:

(1) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, remainder Cu, and unavoidable impurities;
(2) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, remainder Cu, and unavoidable impurities;
(3) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.05 to 5 weight % of Sn and/or Ag, remainder Cu, and unavoidable impurities;
(4) a pitting corrosion resistant piping for supplying hot and cold water, the piping being-made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.05 to 5 weight % of Sn and/or Ag, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R (hereafter, R denotes rare earth elements except Y), remainder Cu, and unavoidable impurities;
(5) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.05 to 5 weight % of Sn and/or Ag, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(6) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.05 to 5 weight % of Sn and/or Ag, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(7) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, remainder Cu, and unavoidable impurities;
(8) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(9) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of Y and/or Zr, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(10) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.05 to 5 weight % of Sn and/or Ag, remainder Cu, and unavoidable impurities;
(11) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.05 to 5 weight % of Sn and/or Ag, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, remainder Cu, and unavoidable impurities;
(12) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.05 to 5 weight % of Sn and/or Ag, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;

(13) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.05 to 5 weight % of Sn and/or Ag, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(14) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, remainder Cu, and unavoidable impurities;
(15) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(16) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising a total amount of 0.005 to 5 weight % of Nb and/or Ta, 0.003 to 0.5 weight % of W, remainder Cu, and unavoidable impurities;
(17) a pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy in which 0.005 to 0.5 weight % of P is added to any one of the copper alloys defined in the above (1) to (16).

There is described next why the composition of the alloy copper for the piping according to the invention is defined as above.

(a) Nb, Ta

Nb and Ta are both active metals. When being added to Cu, Nb and Ta act to reduce the potential and to suppress the occurrence and progress of the pitting corrosion by concentrating on the surface to form a stable oxide layer. If the content of Nb and Ta is less than 0.005 weight %, a satisfactory pitting corrosion preventing effect cannot be obtained because the potential of the copper alloy piping cannot be reduced sufficiently and the oxide layer cannot be formed sufficiently stably. On the other hand, a content of Nb and Ta of more than 5 weight % is not preferable because the pitting corrosion preventing effect is not further enhanced and the productivity is reduced due to the increased melting temperature. Therefore, the range of the amount of Nb and/or Ta is determined to 0.005 to 5 weight %. When Nb and Ta are oxidized through the corrosion reaction, they concentrate between a cuprous oxide layer formed on the surface of the copper alloy piping and the surface of the copper alloy piping and protect the surface of the copper alloy piping. Further, existing in the cuprous oxide layer, Nb and Ta act to improve the stability of the cuprous oxide layer and to suppress the cuprous oxide layer from being oxidized into a copper oxide layer by the action of an oxidizing agent such as the residual chlorine. Thus, Nb and Ta have a function of preventing the occurrence of pitting corrosion. Even if pitting corrosion occurs, its progress is remarkably suppressed since Cu is caused to dissolve preferentially at the bottom of the pitting and the stable oxide layer is formed on the surface of the alloy by the action of Nb and Ta.

A preferable range of the amount of Nb and/or Ta is 0.01 to 0.2 weight %.

(b) Y, Zr

Y and Zr are both active metals. When being added to Cu, Y and Zr act to reduce the potential and to suppress the occurrence and progress of pitting corrosion by concentrating on the surface to form a stable oxide layer. If the content of Y and Zr is less than 0.005 weight %, a satisfactory pitting corrosion preventing effect cannot be obtained because the potential of the copper alloy piping cannot be reduced sufficiently and the oxide layer cannot be formed sufficiently stably. On the other hand, a content of Y and Zr of more than 1 weight % is not preferable because the pitting corrosion preventing effect is not further enhanced and the productivity is reduced due to the increased melting temperature. Therefore, the range of the amount of Y and/or Zr is determined to 0.005 to 1 weight %. When Y and Zr are oxidized through the corrosion reaction, they concentrate between a cuprous oxide layer formed on the surface of the copper alloy piping and the surface of the copper alloy piping and protect the surface of the copper alloy piping. Further, existing in the cuprous oxide layer, Y and Zr act to improve the stability of the cuprous oxide layer and to suppress the cuprous oxide layer from being oxidized into a copper oxide layer by the action of an oxidizing agent such as the residual chlorine. Thus, Y and Zr have a function of preventing the occurrence of the pitting corrosion. Even if the pitting corrosion occurs, its progress is remarkably suppressed since Cu is caused to dissolve preferentially at the bottom of the pitting and the stable oxide layer is formed on the surface of the alloy by the action of Y and Zr.

A preferable range of the amount of Y and/or Zr is 0.03 to 0.3 weight %.

(c) Sn, Ag

Both Sn and Ag act to form a stable oxide and to suppress the occurrence and progress of pitting corrosion. Even if pitting corrosion occurs, Cu is caused to dissolve preferentially at the bottom of the pitting and these elements concentrate on the surface, with the result that the potential is reduced and the stability of the oxide layer is enhanced. This leads to the suppression of the cathodic reaction, thereby blocking and suppressing the progress of the pitting corrosion. Accordingly, the addition of Sn and Ag remarkably intensifies the tendency to change the form of corrosion of the copper alloy piping from the localized corrosion to the entire surface corrosion, and the corrosion extends more in the surface direction rather than in the depth direction. Thus, the corroded portion is more shallow and covers a greater area. However, when the content of Sn and Ag is less than 0.05 weight %, the pitting corrosion suppressing effect is not sufficient because the oxide layer stabilizes the inner surface of the copper alloy piping only insufficiently. On the contrary, a content of Sn and Ag of more than 5 weight % leads to reduced workability. Thus, the content of the sum of Sn and Ag is determined to 0.05 to 5 weight %.

A preferable range of the content of Sn and Ag is 0.2 to 2 weight %.

(d) Ti, R (rare earth elements except Y)

Ti and R act to reduce the potential of the copper alloy and concentrate on the surface of the copper alloy to further enhance the stability of the surface oxide layer, thereby suppressing the occurrence of pitting corrosion. However, a content of Ti and R of less than 0.005 weight % is not sufficient to bring about the increased stability of the surface oxide layer. On the contrary, it is recognized that a content of these elements of more than 1 weight % brings about no further improvement in the pitting corrosion resistance, but a reduced workability. Thus, the content of the sum of Ti and R is determined to 0.005 to 1 weight %.

A preferable range of the content of Ti and R is 0.03 to 0.3 weight %.

(e) W

W is an active metal. When being added to Cu, W acts to reduce the potential of the copper alloy and concentrates on the surface of the copper alloy to form a stable oxide layer, thereby suppressing the occurrence and progress of pitting corrosion. However, when the content of W is less than 0.003 weight %, a sufficient pitting corrosion preventing effect cannot be obtained because the potential of the copper alloy piping cannot be reduced sufficiently and the oxide layer cannot be formed sufficiently stably. On the other hand, a content of W of more than 0.5 weight % is not preferable because the pitting corrosion preventing effect is not further enhanced and the productivity is reduced due to the increased melting temperature. Therefore, the range of the content of W is determined to 0.003 to 0.5 weight %. When being oxidized through the corrosion reaction, W concentrates between a cuprous oxide layer formed on the surface of the copper alloy piping and the surface of the copper alloy piping and protects the surface of the copper alloy piping. Further, existing in the cuprous oxide layer, W acts to improve the stability of the cuprous oxide layer and to suppress the cuprous oxide layer from being oxidized into a copper oxide layer by the action of an oxidizing agent such as the residual chlorine. Thus, W has a function of preventing the occurrence of pitting corrosion. Even if pitting corrosion occurs, W causes Cu to dissolve preferentially at the bottom of the pitting and concentrates on the surface of the copper alloy, thereby forming a stable oxide layer containing mainly W. Such a stable oxide layer stops the progress of the pitting corrosion.

A preferable range of the content of W is 0.01 to 0.1 weight %.

(f) P

Since P has a deoxidizing action, the addition of P facilitates the production of a stable mass of alloy. Further, pitting corrosion often occurs at a surface defect due to oxides undesirably included in the alloy as a starting point. In this respect, the addition of P serves to indirectly suppress the occurrence and progress of pitting corrosion. However, when the content of P is less than 0.005 weight %, the deoxidizing effect is not sufficient, and the oxides included in the mass of alloy cause a defect from which the pitting corrosion starts. The insufficient deoxidizing effect leads to an insufficient pitting corrosion suppressing effect. On the contrary, a content of P of more than 0.5 weight % leads to the formation of phosphates, which reduces the workability considerably and prevents any further improvement in the pitting corrosion resistance. Thus, the content of P is determined to 0.005 to 0.5 weight %. A preferable range thereof is 0.005 to 0.04 weight %.

It will be appreciated that, even if Pb, Bi, As, Fe, Se, Al, S, Sb or the like, each being of less than several ppm, and oxygen of about 50 ppm are included as impurities in the copper alloy used for the cold and hot water supply piping according to the invention, the pitting corrosion resistance is not adversely affected.

BEST MODE FOR EMBODYING THE INVENTION

There were manufactured hot and cold water supply pipings having pitting corrosion resistance according to the invention (hereinafter referred to as inventive copper alloy pipings) 1 to 90, comparative cold and hot water supply pipings having pitting corrosion resistance (hereinafter referred to as comparative copper alloy pipings) 1 to 12, and conventional cold and hot water supply pipings having pitting corrosion resistance (hereinafter referred to as conventional copper alloy pipings) 1 and 2. These pipings were made of copper alloy having the composition shown in TABLE-1 to TABLE-7, the outside diameter thereof being 15.88 mm, the thickness thereof 1.02 mm, and the length thereof 1000 mm.

In any one of the comparative copper alloy pipings 1 to 12, the amount of one of the components falls outside the range according to the invention (such components are shown in TABLE-7 marked with *).

The following water running test was conducted for the inventive copper alloy pipings 1 to 90, the comparative copper alloy pipings 1 to 12, and the conventional copper alloy pipings 1 and 2. Hot water of pH = 7 and 60 °C containing:

Hydrogen carbonate ion	40 mg/l
Sulfate ion	80 mg/l
Chlorine ion	20 mg/l
Sodium silicate	15 mg/l (as SiO_2)
Residual chlorine concentration	5 mg/l

was caused to run at a flow velocity of 1 m/s for one year. The corrosive state of each copper alloy piping after one year was examined by measuring the maximum depth of the cavity and counting the number of cavities formed per unit area. The measurement results are shown in TABLE-1 to TABLE-7.

In the water running test, chlorine was not added for 3 days after the start of the test so as to provide an induction period during which a stable Cu_2O layer is formed on the inner surface of each copper alloy piping. The chlorine was added gradually for 2 days from the fourth day of the test, and the final residual chlorine concentration was 5 mg/l.

TABLE-1

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES (#/dm²)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	1	0.007	-	-	-	-	-	-	-	-	0.001	REM.	165	25
	2	0.05	-	-	-	-	-	-	-	-	-	REM.	110	18
	3	0.1	-	-	-	-	-	-	-	-	-	REM.	95	14
	4	0.5	-	-	-	-	-	-	-	-	-	REM.	115	16
	5	1.0	-	-	-	-	-	-	-	-	-	REM.	105	11
	6	5.0	-	-	-	-	-	-	-	-	-	REM.	90	15
	7	-	0.007	-	-	-	-	-	-	-	0.001	REM.	160	28
	8	-	0.05	-	-	-	-	-	-	-	-	REM.	85	17
	9	-	0.1	-	-	-	-	-	-	-	-	REM.	95	13
	10	-	0.5	-	-	-	-	-	-	-	-	REM.	70	12
	11	-	1.0	-	-	-	-	-	-	-	-	REM.	85	18
	12	-	5.0	-	-	-	-	-	-	-	-	REM.	90	16
	13	0.1	0.3	-	-	-	-	-	-	-	0.001	REM.	75	14
	14	0.7	0.1	-	-	-	-	-	-	-	-	REM.	75	12
	15	0.8	0.07	-	-	-	-	-	-	-	-	REM.	80	15

(REM. denotes remainder)

TABLE-2

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES ($\#/dm^2$)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	16	0.1	-	0.03	-	-	-	-	-	-	-	REM.	65	9
	17	-	0.1	0.05	-	-	-	-	-	-	-	REM.	65	8
	18	0.3	-	0.1	-	-	-	-	-	-	-	REM.	55	4
	19	-	0.3	0.006	-	-	-	-	-	-	0.001	REM.	60	5
	20	0.2	-	0.8	-	-	-	-	-	-	-	REM.	50	4
	21	-	0.1	0.1	0.005	-	-	-	-	-	-	REM.	45	2
	22	0.1	0.1	0.1	0.05	-	-	-	-	-	-	REM.	45	3
	23	0.1	0.1	-	0.1	-	-	-	-	-	-	REM.	50	3
	24	0.05	0.07	-	0.3	-	-	-	-	-	-	REM.	45	4
	25	0.08	0.02	-	0.9	-	-	-	-	-	-	REM.	50	2
	26	0.1	-	-	-	0.05	-	-	-	-	0.001	REM.	60	2
	27	-	0.1	-	-	1.0	-	-	-	-	-	REM.	50	3
	28	0.1	-	-	-	4.0	-	-	-	-	-	REM.	65	3
	29	0.1	0.1	-	-	0.5	0.5	-	-	-	-	REM.	45	2
	30	-	0.1	-	-	-	0.05	-	-	-	0.001	REM.	75	10

(REM. denotes remainder)

TABLE-3

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES (#/dm²)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	31	0.1	-	-	-	-	1.0	-	-	-	-	REM.	80	11
	32	-	0.1	-	-	-	3.0	-	-	-	-	REM.	65	7
	33	0.1	-	-	-	-	5.0	-	-	-	-	REM.	60	5
	34	0.1	0.1	-	-	-	-	0.005	-	-	0.001	REM.	95	17
	35	0.1	-	-	-	-	-	0.03	-	-	-	REM.	80	16
	36	-	0.1	-	-	-	-	0.1	-	-	-	REM.	80	10
	37	0.1	0.05	-	-	-	-	0.9	-	-	-	REM.	70	8
	38	0.1	-	-	-	-	-	-	0.007	-	0.001	REM.	130	20
	39	-	0.1	-	-	-	-	-	0.05	-	-	REM.	95	19
	40	0.1	-	-	-	-	-	-	0.3	-	-	REM.	90	15
	41	-	0.09	-	-	-	-	-	0.8	-	-	REM.	80	13
	42	0.005	0.005	-	-	-	-	0.04	0.01	-	-	REM.	85	12
	43	0.005	0.5	-	-	-	-	-	-	0.005	0.001	REM.	115	15
	44	0.005	-	-	-	-	-	-	-	0.05	-	REM.	125	14
	45	0.1	-	-	-	-	-	-	-	0.1	-	REM.	120	15

(REM. denotes remainder)

TABLE-4

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES (#/dm²)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	46	-	0.1	-	-	-	-	-	-	0.5	-	REM.	95	14
	47	0.1	0.1	-	-	-	-	-	-	-	0.005	REM.	85	11
	48	0.1	-	-	-	-	-	-	-	-	0.01	REM.	80	10
	49	-	0.1	-	-	-	-	-	-	-	0.04	REM.	80	12
	50	0.1	-	-	-	-	-	-	-	-	0.5	REM.	70	9
	51	0.1	-	0.1	-	1.0	-	-	-	-	-	REM.	45	3
	52	0.1	-	-	0.1	-	1.0	-	-	-	-	REM.	50	4
	53	0.1	0.1	0.1	0.1	0.8	-	-	-	-	0.001	REM.	30	2
	54	-	0.1	0.1	-	1.2	-	0.1	-	-	-	REM.	30	2
	55	0.1	0.1	0.5	-	0.5	-	-	0.1	-	0.001	REM.	35	3
	56	0.1	0.1	-	0.5	-	1.0	0.1	0.05	-	-	REM.	25	3
	57	0.1	-	0.1	-	1.5	-	0.1	-	0.1	0.001	REM.	20	2
	58	-	0.1	0.05	0.05	0.1	-	0.1	-	0.01	-	REM.	40	5
	59	0.1	-	-	0.1	1.0	-	0.1	-	0.05	-	REM.	30	3
	60	-	0.1	0.1	-	-	1.5	-	-	0.03	-	REM.	25	3

(REM. denotes remainder)

TABLE-5

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES (#/dm^2)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	61	0.1	-	0.1	-	1.0	-	-	-	0.01	-	REM.	55	5
	62	0.1	-	-	0.1	-	0.5	-	-	0.07	-	REM.	60	6
	63	-	0.1	-	0.1	-	-	0.1	-	-	0.005	REM.	70	6
	64	0.1	-	-	0.1	-	-	-	0.1	-	-	REM.	65	4
	65	-	0.1	-	0.1	-	-	-	0.03	-	-	REM.	70	7
	66	0.1	0.1	0.1	-	-	-	0.3	-	-	-	REM.	55	5
	67	0.1	-	0.05	0.05	-	-	0.1	-	0.01	-	REM.	60	4
	68	-	0.1	0.1	-	-	-	-	0.1	0.05	-	REM.	55	3
	69	0.05	0.05	-	0.1	-	-	0.05	0.05	0.01	-	REM.	65	3
	70	0.1	-	0.1	-	-	-	-	-	0.03	-	REM.	60	4
	71	-	0.1	-	0.05	-	-	-	-	0.1	-	REM.	60	3
	72	0.1	-	-	0.1	-	-	-	-	0.009	0.005	REM.	70	5
	73	0.5	-	-	-	1.0	-	-	-	0.05	-	REM.	65	3
	74	-	0.1	-	-	-	1.1	-	-	0.01	0.005	REM.	50	6
	75	0.1	-	-	-	2.0	-	-	-	0.01	-	REM.	35	2

(REM. denotes remainder)

TABLE-6

COPPER ALLOY PIPING		COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES ($\#/dm^2$)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
INVENTION	76	0.1	0.1	-	-	-	0.5	0.1	-	-	0.01	REM.	55	4
	77	0.1	-	-	-	2.0	-	-	0.1	-	-	REM.	45	3
	78	-	0.1	-	-	0.5	0.5	0.1	0.1	-	-	REM.	50	3
	79	0.1	-	-	-	1.0	-	0.1	-	0.01	-	REM.	50	4
	80	0.1	-	-	-	-	1.0	-	0.1	0.05	-	REM.	55	6
	81	-	0.1	-	-	0.5	0.5	0.1	0.1	0.08	-	REM.	40	3
	82	0.1	0.1	-	-	1.0	-	-	0.1	0.1	-	REM.	35	2
	83	0.1	-	-	-	1.0	-	0.1	-	0.05	0.01	REM.	40	3
	84	-	0.1	-	-	-	1.0	0.1	-	0.05	0.02	REM.	40	5
	85	0.1	0.1	-	-	1.0	-	0.05	0.05	0.1	0.03	REM.	45	5
	86	0.1	-	-	-	0.5	0.5	-	0.15	0.1	0.01	REM.	35	3
	87	0.1	-	-	-	-	0.5	0.01	0.01	0.01	0.01	REM.	30	2
	88	0.1	0.1	-	-	-	-	0.1	-	0.1	-	REM.	85	9
	89	0.1	-	-	-	-	-	-	0.1	0.1	-	REM.	75	9
	90	-	0.1	-	-	-	-	0.1	0.1	0.1	0.008	REM.	70	7

(REM. denotes remainder)

TABLE-7

	COPPER ALLOY PIPING	COMPOSITION (WEIGHT %)											MAX. DEPTH OF CAVITY (μm)	NUMBER OF CAVITIES (#/dm²)
		Nb	Ta	Y	Zr	Sn	Ag	Ti	R	W	P	Cu		
COMPARATIVE EXAMPLE	1	0.003*	-	-	-	-	-	-	-	-	-	REM.	690	150
	2	-	0.003*	-	-	-	-	-	-	-	-	REM.	760	165
	3	7.0*	-	-	-	-	-	-	-	-	-	REM.	70♦	3♦
	4	-	7.0*	-	-	-	-	-	-	-	-	REM.	75♦	3♦
	5	0.1	-	1.5*	-	-	-	-	-	-	-	REM.	53♦	1♦
	6	-	0.1	-	1.5*	-	-	-	-	-	-	REM.	54♦	2♦
	7	0.1	-	-	-	6.2*	-	-	-	-	-	REM.	55♦	1♦
	8	-	0.1	-	-	-	6.0*	-	-	-	-	REM.	60♦	1♦
	9	0.1	0.1	-	-	-	-	1.5*	-	-	-	REM.	50♦	1♦
	10	0.1	-	-	-	-	-	-	1.5*	-	-	REM.	65♦	2♦
	11	0.1	-	-	-	-	-	-	-	1.5*	-	REM.	73♦	2♦
	12	0.1	-	-	-	-	-	-	-	-	0.7*	REM.	75♦	3♦
PRIOR ART	1	P : 0.025				Sn : 0.5		Al : 1.2				REM.	680	210
	2	P : 0.027				Sn : 0.3		Al : 1.2				REM.	850	245

(Values marked with * fall outside the range according to the invention. ♦ denotes poor workability and weldability despite good pitting corrosion resistance and REM. denotes remainder)

In consideration of how the pitting corrosion of Type II occurs, the above water running test is better in reliably reproducing the occurrence of pitting corrosion than the conventional tests in which the chlorine is added simultaneously with the start of the test. In other words, if the residual chlorine concentration in the test water (hot water) is set high from the beginning of the test, there is a danger that surface corrosion rather than pitting corrosion occurs and the pitting corrosion resistance of the copper alloy piping cannot be evaluated accurately.

From the results shown in TABLE-1 to TABLE-7, it is seen that the inventive copper alloy pipings 1 to 90, which are made of the copper alloy containing a total amount of 0.005 to 5 weight % (preferably 0.01 to 0.2 weight %) of Nb and/or Ta as essentials, have a better pitting corrosion resistance than the conventional copper alloy pipings 1 and 2. The copper alloy used for the inventive pipings may contain further, if desired, one or more of:

(i) a total amount of 0.005 to 5 weight % (preferably 0.03 to 0.3 weight %) of Y and/or Zr;

(ii) a total amount of 0.05 to 5 weight % (preferably 0.2 to 2 weight %) of Sn and/or Ag;

(iii) a total amount of 0.005 to 1 weight % (preferably 0.03 to 0.3 weight %) of one or more elements selected from Ti and R; and

(iv) 0.003 to 0.5 weight % (preferably 0.01 to 0.1 weight %) of W.

This copper alloy may furthermore contain, if desired, 0.005 to 0.5 weight % (preferably 0.005 to 0.04 weight %) of P.

As seen in the comparative copper alloy pipings 1 and 2, the pitting corrosion resistance decreases when the content of Nb and/or Ta is less than a lower limit of the range according to the invention. As seen in the comparative copper alloy pipings 3 and 4, an excessive content of Nb and Ta leads to an exceedingly reduced workability and/or weldability despite an improved pitting corrosion resistance. It is difficult to manufacture a piping by using the copper alloy in which Nb and/or Ta are excessively added. Even if such copper alloy can be manufactured into a pipe, this pipe cannot be used in a piping since it cannot be bent or worked by plastic deformation. Further, since weldability is also reduced, it becomes difficult to connect the pipings. Thus, the excessive addition of these elements causes the piping to have undesirable properties.

As seen from the comparative copper alloy pipings 5 to 12, an excessive addition of any desired element other than Nb and Ta is not preferable, because workability and/or weldability are reduced although the pitting corrosion resistance is increased.

In this example, the test was conducted using the water which causes the pitting corrosion of Type II, but it was also confirmed that the copper alloy piping according to the invention demonstrates an excellent pitting corrosion resistance against such water that causes the pitting corrosion of Type I.

As described above, a copper alloy piping according to the invention has a much better pitting corrosion resistance than that of the prior art. When the copper alloy according to the invention is used for a pitting corrosion resistant piping for supplying hot and cold water, e.g., in hotels, hospitals and apartment houses, the reliability against pitting corrosion will be more enhanced than before.

Claims

1. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
remainder Cu, and
unavoidable impurities.

2. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
remainder Cu, and
unavoidable impurities.

3. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
remainder Cu, and
unavoidable impurities.

4. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,

remainder Cu, and
unavoidable impurities.

5. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
remainder Cu, and
unavoidable impurities.

6. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
remainder Cu, and
unavoidable impurities.

7. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R (hereafter, R denotes rare earth elements except Y),
remainder Cu, and
unavoidable impurities.

8. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

9. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

10. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

11. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

12. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

13. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

14. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

15. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

16. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

17. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:

a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of Y and/or Zr,
0.003 to 0.5 weight % of W,
remainder Cu, and

unavoidable impurities.

18. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of Y and/or Zr,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

19. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
remainder Cu, and
unavoidable impurities.

20. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
remainder Cu, and
unavoidable impurities.

21. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

22. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

23. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

24. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

25. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.05 to 5 weight % of Sn and/or Ag,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

26. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.2 to 2 weight % of Sn and/or Ag,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

27. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

28. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
remainder Cu, and
unavoidable impurities.

29. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
a total amount of 0.005 to 1 weight % of one or more elements selected from Ti and R,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

30. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
a total amount of 0.03 to 0.3 weight % of one or more elements selected from Ti and R,
0.01 to 0.1 weight % of W,
remainder Cu, and
unavoidable impurities.

31. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.005 to 5 weight % of Nb and/or Ta,
0.003 to 0.5 weight % of W,
remainder Cu, and
unavoidable impurities.

32. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy comprising:
a total amount of 0.01 to 0.2 weight % of Nb and/or Ta,
0.01 to 0.1 weight % of W,
remainder Cu, and

unavoidable impurities.

33. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy in which 0.005 to 0.5 weight % of P is added to any one of the copper alloys defined in claims 1 to 32.

34. A pitting corrosion resistant piping for supplying hot and cold water, the piping being made of copper alloy in which 0.005 to 0.04 weight % of P is added to any one of the copper alloys defined in claims 1 to 32.

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP93/01846

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 C22C9/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^5 C22C9/00, E03B7/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1993
Kokai Jitsuyo Shinan Koho 1971 - 1993

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP, A, 63-310932 (Kurasawa Kogaku kogyo K.K.), December 19, 1988 (19. 12. 88), Lines 17 to 19, lower right column, page 1, (Family: none)	1 2-34
Y	JP, B2, 5-25931 (The Furukawa Electric Co., Ltd.), April 14, 1993 (14. 04. 93), Lines 7 to 10, column 3, (Family: none)	3-18
A	JP, B2, 58-39900 (Mitsubishi Metal Corp.), September 2, 1983 (02. 09. 83), Line 16, column 3 to line 1, column 1, (Family: none)	33-34
X	JP, B2, 59-53142 (Asahi Chemical Industry Co., Ltd.), December 24, 1984 (24. 12. 84), (Family: none)	27-28
A	JP, B2, 58-54180 (Mitsui Metal & Mining Co., Ltd.),	5-12

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
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- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
March 17, 1994 (17. 03. 94)	April 5, 1994 (05. 04. 94)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/01846

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	December 3, 1983 (03. 12. 83), Lines 8 to 28, column 2, (Family: none)	
A	JP, B2, 60-20454 (Nippon Mining Co., Ltd.), May 22, 1985 (22. 05. 85), Lines 9 to 13, column 2, (Family: none)	3-18, 21-24, 27-30
A	JP, A, 62-218534 (The Furukawa Electric Co., Ltd.), September 25, 1987 (25. 09. 87), (Family: none)	1-34
A	JP, A, 62-240752 (Furukawa Electric Co., Ltd.), October 21, 1987 (21. 10. 87), (Family: none)	1-34
A	JP, A, 63-293129 (Furukawa Electric Co., Ltd.), November 30, 1988 (30. 11. 88), (Family: none)	1-34