(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 440 548 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **91400200.1**

(51) Int. Cl.[5]: **H01R 13/03**

(22) Date of filing: **29.01.91**

(30) Priority: **30.01.90 JP 19719/90**

(43) Date of publication of application:
07.08.91 Bulletin 91/32

(84) Designated Contracting States:
FR GB NL

(71) Applicant: **KABUSHIKI KAISHA KOBE SEIKO SHO also known as Kobe Steel Ltd.
3-18 1-chome, Wakinohama-cho Chuo-ku
Kobe 651 (JP)**

(72) Inventor: **Miyafuji, Motohisa
2-5-8, Anyoji, Chofu, Shimonoseki-shi
Yamaguchi-ken (JP)**
Inventor: **Hosokawa, Isao
4-1, Nakadoihon-machi, Chofu
Shimonoseki-shi, Yamaguchi-ken (JP)**

(74) Representative: **Rodhain, Claude et al
Cabinet Claude Rodhain 30, rue la Boétie
F-75008 Paris (FR)**

(54) **Migration-resistant copper alloy for terminal and connector uses having excellent spring characteristics, strength and conductivity.**

(57) Disclosed herein is a migration-resistant copper alloy for terminal and connector uses having excellent spring characteristics, strength and conductivity which contains 0.4 to 4.0% by weight of Ni, 0.1 to 1.0% by weight of Si, 1.0% (exclusive) to 5.0% (inclusive) by weight of Zn, 0.05 to 0.5% by weight of Mg, 0.1 to 0.5% by weight of Sn, and 0.001% (inclusive) to 0.01% (exclusive) by weight of at least one of Cr, Ti and Zr, the balance being Cu and unavoidable impurities. The copper alloy is excellent in softening resistance, migration resistance, stress relaxation properties, corrosion resistance, etc. as well as spring characteristics, strength and conductivity, and is suitable for terminals and connectors.

EP 0 440 548 A2

MIGRATION-RESISTANT COPPER ALLOY FOR TERMINAL AND CONNECTOR USES HAVING EXCELLENT SPRING CHARACTERISTICS, STRENGTH AND CONDUCTIVITY

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a migration-resistant copper alloy for terminal and connector uses which has excellent spring characteristics, strength and conductivity.

(2) Description of the Prior Art

There have been various types of terminals and connectors, for example, those as shown in Figure 4.

In response to the recent needs for electric and electronic apparatus smaller in weight and dimensions, the component parts used for electric and electronic apparatus have also come to be reduced in size. The reduction in size of the component parts has been accompanied by a closer pitch of electrodes, an increase in the number of electrodes and, further, an increased current capacity, in designing the terminals and connectors.

Conventionally, brass or phosphor bronze alloys have been used as materials for terminals and connectors. However, the brass or phosphor bronze alloys, when used as a terminal or connector material, have the following drawbacks.

The conductivity of brass is as low as 28% IACS, and that of phosphor bronze alloys is as low as 22% IACS. In addition, these materials are poor in heat resistance.

Further, the terminals or connectors made of brass or a phosphor bronze alloy become unable to exhibit their intended function, because of a lowering in the fitting force at the joint portion in use. Such a lowering of fitting force is probably due to the vast quantity of Joule heat generated by an increased current flowing through the terminal or connector.

In addition to the above, the phosphor bronze alloys have the problem of poor resistance to migration. The migration, here, is a phenomenon in which copper (Cu) ionized upon dew deposition or the like between electrodes is urged by the Coulomb force between the electrodes to deposit on the cathode, and crystals of the deposited metal grows in a dendritic form from the cathode, in the same manner as in electrodeposition, to eventually reach the anode, resulting in short-circuit. Such a phenomenon arises from repeated dew deposition and drying. Although the migration has formerly known to occur on Ag, it has been known that the migration also occurs on phosphor bronze alloys, according to the above-mentioned closer electrode spacing or the like.

On the other hand, brass has the problem of poor resistance to stress corrosion cracking, it has excellent migration resistance.

Thus, there has hitherto been no material that is excellent in conductivity, strength, elastic limit, fitting force and migration resistance, is also excellent in corrosion resistance, especially resistance to stress corrosion cracking and that is capable of coping with the problem of increased current capacity associated with the smaller size and higher density of terminals and connectors and with the worsening use environment for the terminals and connectors.

SUMMARY OF THE INVENTION

It is accordingly an object of this invention to provide a cooper alloy for terminal and connector uses which has excellent conductivity, strength, spring characteristics, fitting force and migration resistance and is excellent in corrosion resistance, particularly resistance to stress corrosion cracking.

According to this invention, there is provided a migration-resistant copper alloy for terminal and connector uses having excellent spring characteristics, strength and conductivity which contains 0.4 to 4.0% by weight of Ni, 0.1 to 1.0% by weight of Si, 1.0% (exclusive) to 5.0% (inclusive) by weight of Zn, 0.05 to 0.5% by weight of Mg, 0.1 to 0.5% by weight of Sn, and 0.001% (inclusive) to 0.01% (exclusive) by weight of at least one of Cr, Ti and Zr, the balance being Cu and unavoidable impurities.

The alloy of this invention is excellent in spring limit, conductivity, softening resistance, migration resistance, relaxation properties, etc. as well as strength, and is therefore suitable for terminals and connectors.

The above and other objects, features and advantages of this invention will become apparent from the following description and appended claims, taken in conjunction with the accompanying drawing which show by way of example some preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are each a conceptual illustration of a testing method for migration resistance ;
Figure 3 is a conceptual illustration of a measuring method for stress relaxation ; and
Figure 4 shows sectional views and perspective views of exemplar terminals and connectors.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the copper alloy according to this invention, the aforementioned constituents are contained in the aforementioned respective amounts, the limits of which are set on the grounds as follows.

Ni

Nickel (Ni), when added to the alloy together with Si, improves strength of the alloy. When the Ni content of the alloy is less than 0.4% by weight, an improved strength cannot be expected even if the alloy contains Si in an amount of 0.1 to 1.0% by weight. When the Ni content is more than 4.0% by weight, the workability of the copper alloy is worsened, and the strength of the alloy is little improved. Therefore, the Ni content is set in the range of 0.4 to 4.0% by weight.

Si

Silicon (Si) improves the strength of the copper alloy by forming a compound with Ni. When the Si content is less than 0.1% by weight, improvement of strength is not expectable even if the alloy contains 0.4 to 4.0% by weight of Ni. An addition of more than 1.0% by weight of Si, on the other hand, lowers workability and conductivity of the alloy. Thus, the Si content is set in the range from 0.1 to 1.0% by weight.

Zn

Wettability by solder and tin and adhesion to solder and tin are essential to materials for electronic apparatus. Zinc (Zn) is an indispensable element for inhibition of peeling of solder and Sn platings and for improvement of migration resistance.

Upon penetration of water, dew deposition or the like between electrodes of an electric or electronic component part, zinc prevents the development of migration of Cu, because of the difference in electrochemical tendency between Zn and Cu, thereby suppressing leakage current. If the Zn content is not more than 1.0% by weight, the cooper alloy cannot have properties comparable to those of brass. On the other hand, an addition of more than 5.0% by weight of Zn leads to unfavorable results such as a lower conductivity and lower resistance to stress corrosion cracking, though the migration resistance of the alloy is improved. Therefore, the Zn content is set in the range from 1.0% (exclusive) to 5.0% (inclusive) by weight.

Mg

Magnesium (Mg) is an indispensable element for improving the hot workability and strength, particularly spring limit, of the copper alloy. When added in an amount of not less than 0.05% by weight, magnesium reacts with sulfur, which is introduced into the copper alloy from the raw materials at the time of ingot casting and which has a low melting point. The reaction yields MgS, which has a high melting point. Thus, magnesium fixes sulfur, thereby improving hot workability of the copper alloy and, further, enhancing the spring limit of the alloy. When the Mg content exceeds 0.5% by weight, however, the improvement of spring limit is saturated and, rather, there results a lowering in the fluidity and casting qualities at the time of melting and casting the cooper alloy. Therefore, the Mg content is set in the range of 0.05 to 0.5% by weight.

Sn

Tin (Sn) improves the strength and spring limit of the copper alloy, by dissolving in Cu. When the Sn content is less than 0.1% by weight, the improvement of strength and spring limit cannot be expected, whereas an addition of more than 0.5% by weight of Sn leads to a lower conductance. Thus, the Sn content is set in the range of 0.1 to 0.5% by weight.

Cr, Ti, Zr

Chromium (Cr), titanium (Ti) and zirconium (Zr) each function to strengthen the grain boundaries of an ingot of the copper alloy and to improve the hot workability of the alloy. When the amount of these elements added is less than 0.001% by weight, the effect of the addition is slight, whereas an addition of more than 0.01% by weight of these elements leads to easier oxidation of the molten alloy, thereby making it impossible to obtain a sound ingot. Therefore, at least one of Cr, Ti and Zr is contained in an amount of 0.001% (inclusive) to 0.01% (exclusive) by weight.

Production Example

The copper alloy of this invention can be produced, for example, by the following process.

An ingot of the alloy of this invention is made by the conventional semi-continuous casting method, and is hot worked at a temperature of 900 to 970°C. The hot working is followed by quenching from a temperature of not lower than 650°C, at a cooling rate of at least 15°C/sec. When the temperature from which to quench the hot-worked alloy is lower than 600°C, both Ni and Si fail to dissolve in the Cu phase even if the cooling rate is 15°C/sec or above. Similarly, when the cooling rate is below 15°C/sec, both Ni and Si fail to dissolve in the Cu phase even if the alloy is quenched from a temperature of 650°C or above. In such cases, the intended precipitation starts before a precipitation hardening treatment, and the precipitates are aggregated and coarsened, so that the contribution of the precipitates to strength of the alloy is reduced. In view of this, the quenching temperature is 600°C or above, and the cooling rate is at least 15°C/sec.

Subsequently, an at least 30% cold working is conducted, and a precipitation hardening treatment is carried out. The temperature at which a maximum amount of Ni_2Si is precipitated, namely, the temperature which leads to a highest conductance is 500°C. The precipitation amount of the Ni_2Si compound is small at temperatures below 400°C. Therefore, annealing for precipitation hardening is carried out a temperature of 400 to 550°C. When the annealing time is less than 5 minutes, satisfactory precipitation is not effected. On the other hand, an annealing for more than 4 hours is of no use, on an economical basis. Thus, the annealing is carried out for a period of 5 minutes to 4 hours.

Embodiments

Now, some embodiments of the migration-resistant copper alloy for terminal and connector uses having excellent strength and conductivity according to this invention will be explained below.

Alloys having the chemical compositions set forth in Table 1 were melted in air by a resistance heating type electric furnace and under a charcoal covering. From the alloys thus melted, ingots with 50 mm thickness, 80 mm width and 180 mm length were cast.

Next, the face and back surfaces of each ingot were faced about 2 mm, followed by heating to 950°C, hot working down to a 15 mm thickness, reheating to 700°C, and quenching in water. The cooling rate of the quenching was 30°C/sec.

After oxides on the surfaces of the quenched products were removed mechanically, cold rolling down to a 1.2 mm thickness was carried out, and precipitation hardening annealing was carried out at 525°C for 3 hours. The thus treated alloy products were cold rolled down to a 0.36 mm thickness, then precipitation hardening annealing was carried out again, at 475°C for 3 hours, followed by predetermined finish rolling.

Subsequently, low-temperature annealing was carried out at 400°C for the purpose of improving spring limit and elongation.

The specimens prepared as above were subjected to senile tests and to measurement of stress relaxation, spring characteristics, conductivity and softening resistance.

Test pieces for tensile test and measurement of spring characteristics, stress relaxation and conductivity were made to have the longitudinal direction in the rolling direction.

The tensile test was carried out by use of JIS No. 13B test pieces on a 2-ton universal testing machine. spring limit was tested according to JIS H3130.

Electrical conductivity was measured based on JIS H0505.

Migration resistance was tested as follows. A pair of test pieces as shown in Figure 1, 0.64 mm x 3.0 mm x 80 mm, were prepared from each specimen. With a DC voltage of 14 V applied to the pair of test pieces, a drying-wetting test cycle consisting of 5-min immersion in tap water and 10-min drying was repeated 50 times, as shown in Figure 2, and the maximum leak current during the 50 test cycles was measured by a high-sensitivity recorder.

The stress relaxation was determined by measuring the deformation (residual bend) of each test piece after the test piece was maintained at 150°C for 500 hours, with a stress of 80% based on the yield stress of the test piece being exerted thereon, in a cantilever condition, as shown in Figure 3.

The stress relaxation was calculated according to the following formula :

Stress relaxation (%) = $l_1/l_0 \times 100$

where l_0 is the displacement of the test piece upon application of the stress, and l_1 is the displacement of the test piece upon removal of the stress after 500 hours of testing. Besides, l in the figure is the initial position of the test piece before application of the stress.

The results of the above tests, for the alloys of this invention and for comparative alloys, are set forth in Table 2.

Table 1

	No.	Chemical Composition (wt %)									
		Ni	Si	Zn	Mg	Sn	Cr	Ti	Zr	P	Cu
Alloys of this invention	1	1.6	0.32	1.2	0.06	0.1	0.002	—	—	—	Balance
	2	1.6	0.34	3.4	0.20	0.2	—	0.002	—	—	〃
	3	1.6	0.36	4.9	0.34	0.4	—	—	0.003	—	〃
	4	2.4	0.49	1.4	0.14	0.2	—	—	0.002	—	〃
	5	2.4	0.50	2.4	0.26	0.3	0.001	0.003	—	—	〃
	6	3.2	0.70	1.5	0.15	0.2	—	0.002	0.001	—	〃
	7	3.2	0.71	4.0	0.49	0.4	0.002	—	0.002	—	〃
	8	3.2	0.68	4.9	0.28	0.4	0.002	0.001	—	—	〃
Comperative Alloys	9	1.6	0.35	0.2	0.10	—	—	—	—	—	〃
	10	1.6	0.32	2.4	—	—	—	—	—	—	〃
	11	2.4	0.08	1.6	0.14	—	0.002	—	—	—	〃
	12	3.2	0.71	0.70	—	0.05	—	—	0.002	—	〃
	13	3.2	0.65	5.8	—	—	—	—	—	—	〃
	14	—	—	3.0	—	—	—	—	—	—	〃
	15	—	—	—	—	4	—	—	—	0.05	〃

Table 2

	No.	Tensile strength Kgf/mm²	Elongration %	Spring limit Kgf/mm²	Electrical conductivity %IACS	Heat Softening Temperature ℃ ※	Relaxation factor %	Migration Resistance Maximum leak current (A)
Alloys of this invention	1	55.8	9.3	41.5	51	475	12	0.53
	2	56.2	9.6	44.3	44	475	12	0.48
	3	56.5	9.8	45.2	41	480	12	0.47
	4	57.8	10.8	45.8	50	490	11	0.54
	5	62.5	11.5	46.3	48	500	11	0.50
	6	62.8	12.0	47.2	49	500	11	0.51
	7	63.3	12.0	48.7	38	500	11	0.47
	8	63.4	12.2	49.2	39	500	11	0.47
Comparative Alloys	9	54.2	8.7	36	54	475	13	2.50
	10	55.1	8.9	33.5	49	475	13	0.60
	11	57.2	8.5	37.5	52	475	13	0.57
	12	62.8	9.1	31.7	53	500	12	2.85
	13	60.5	9.3	32.0	42	480	16	0.50
	14	59.1	8.8	30.1	28	300	60	0.48
	15	57.6	11.7	38.5	18	375	25	3.80

* Softening resistance temperature : Annealing temperature for 5 min heating at which 80 % of initial hardness is maintained.

Tensile test piece: JIS No. 13B test piece, 0.25 mm[t] thick.

As evident from Table 2, the alloys of this invention are superior in electrical conductivity and softening resistance to brass of No. 14 and phosphor bronze of No. 15, which are comparative alloys. The alloys of this invention are comparable to phosphor bronze as to strength and spiring limit, and are as high a brass in terms of migration resistance.

As has been described above, the migration-resistant copper alloy for terminal and connector uses having excellent strength and conductivity according to this invention is capable of coping with the decreasing size of terminals and connectors, because of its excellent spring limit, electrical conductivity, softening resistance, migration resistance, etc., and ensures less deterioration in the function of the terminals and connectors due to lowered fitting forces at joint portions upon increases in current capacity.

With the copper alloy of this invention used, it is possible to inhibit the migration of Cu which would be caused by condensation of moisture or penetration of water under worsened use conditions for electronic apparatus. As a result, the short-circuit trouble as has been experienced with a smaller electrode pitch is prevented.

Accordingly, the alloy of this invention has a well-balanced combination of conductivity stress relaxation characteristics and migration resistance, as well as excellent spring limit, and is suitable for terminals and connectors. The alloy of this invention, therefore, contributes greatly to electronic and electric machinery industries.

Claims

1. A migration-resistant copper alloy for terminal and connector uses having excellent spring characteristics, strength and conductivity, characterized in that it contains 0.4 to 4.0% by weight of Ni, 0.1 to 1.0% by weight of Si, 1.0% (exclusive to 5.0% (inclusive) by weight of Zn, 0.05 to 0.5% by weight of Mg, 0.1 to 0.5% by weight of Sn, and 0.001% (inclusive) to 0.01% (exclusive) by weight of at least one of Cr, Ti and Zr, the balance being Cu and unavoidable impurities.

FIG. 1

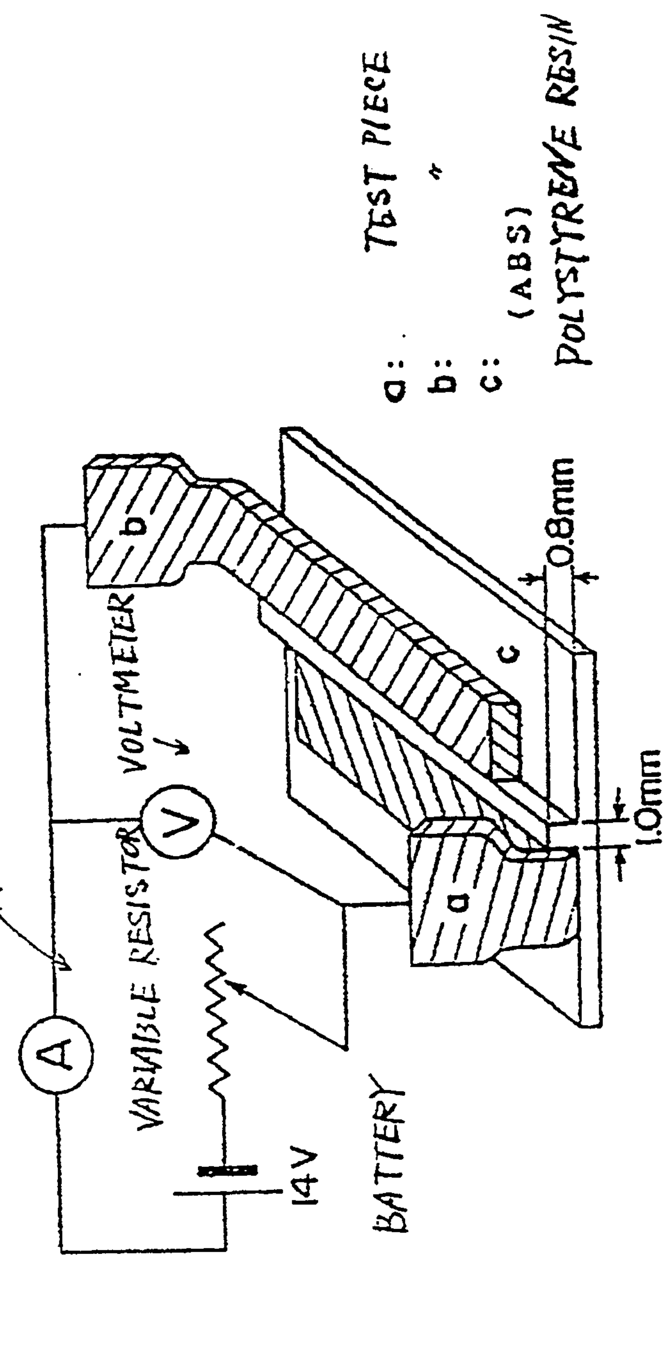
AMMETER
VOLTMETER
VARIABLE RESISTOR
BATTERY
14V
A
V
a
b
c
0.8mm
1.0mm
a: TEST PIECE
b: "
c: (ABS) POLYSTYRENE RESIN

FIG. 2

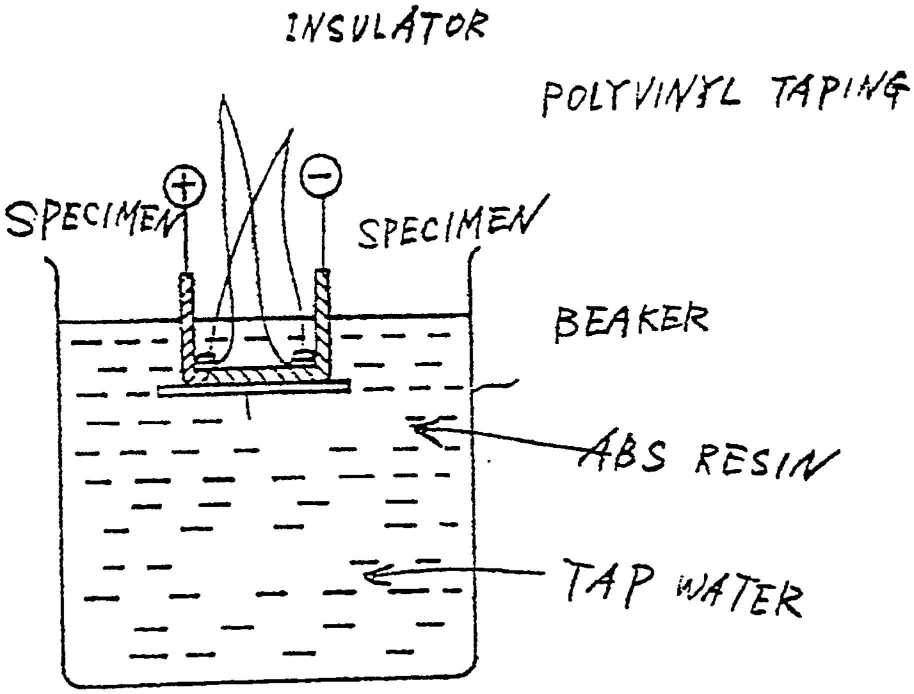
INSULATOR
POLYVINYL TAPING
SPECIMEN
SPECIMEN
BEAKER
ABS RESIN
TAP WATER

FIG. 3

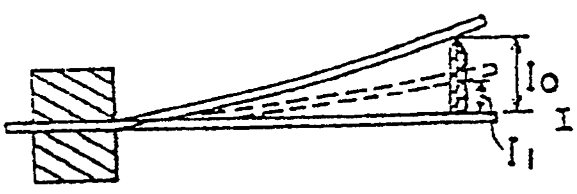
I0
I
I1

FIG. 4