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COPPER ALLOYS FOR ELECTRIC AND ELECTRONIC
DEVICES AND METHOD FOR PRODUCING SAME

This invention relates to copper alloys for electric and electronic devices and to a method for producing the same. More particularly, it relates to copper alloys for electric and electronic devices which have
5 excellent resistance to the peeling of coated tin plating or tin alloy plating and to a method for producing the alloys.

In general, high strength and high conductivity
10 copper alloys are suitable for use in the manufacture of electric and electronic devices. In particular, Cu-Ni-Si alloys have the required characteristics for use in the manufacture of such articles. Alloys for electric and electronic devices are manufactured
15 with a tin plating or solder plating applied, said plating being made of a tin alloy. A problem with conventional tin alloy platings is that they peel or crack, which obviously lessens the reliability of the plated products. In view of this problem, alloy
20 plated electric and electronic devices are subjected, for example, to a high temperature storage test after soldering, in which the soldered alloys are heated to 150°C for 500 hrs in air to determine the resistance of tin and solder platings to peeling. In spite of
25 their high strength and high conductivity there are still problems with the above-mentioned Cu-Ni-Si alloys in that when they are subjected to the high temperature storage test after soldering, the solder is liable to peel. Thus, such alloys have heretofore
30 only had limited use in the manufacture of electric and electronic devices.

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In order to overcome the disadvantages of the conventional alloys, studies have been made in which a variety of elements have been added to Cu-Ni-Si alloys. As a result, it has now been found that
5 incorporation of Zn with or without Cr is effective in improving the peeling resistance of such alloys. Moreover, it has also been found, as the result of X-ray diffraction analysis, that in Cu-Ni-Si alloys, precipitation of large amounts of Ni_2Si contributes
10 to improvement in the peeling resistance of the applied solder. Moreover, it has been ascertained that the annealing temperature of 400°C - 550°C after cold working is the point at which the maximum amount of Ni_2Si precipitates. The annealing time used was in the
15 range of 5 minutes to 4 hours.

Because Cu-Ni-Si alloys are of the precipitation hardening type, their cold workability is greatly influenced by the quenching conditions after hot-working.
20 Accordingly, different quenching conditions have been investigated in order to improve the productivity and to achieve a stable quality, with the result that it has been found that the quenching temperature should be over 600°C with a cooling rate over 15°C per second.

25 Accordingly, the present invention is to provide an alloy for electric and electronic devices which imparts an improved peeling resistance to tin and tin alloy platings.

30 The present invention provides a copper alloy for electric and electronic devices, comprising: 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn and the balance of Cu and
35 the inevitable impurities.

13

- 3 -

The present invention also provides a copper alloy for electric and electronic devices, comprising: 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, 0.005 to 0.1 wt% of Cr, and the balance of Cu and the inevitable impurities.

The present invention also provides a method for producing a copper alloy for electric and electronic devices, comprising the steps of:

a) subjecting to hot working a copper alloy which comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, and the balance Cu and the inevitable impurities ;

b) cooling the alloy at a rate over 15°C per second from a temperature exceeding 600°C ; and

c) after cold working, annealing the alloy at 400°C - 550°C for 5 minutes to 4 hours.

The present invention also provides a method for producing a copper alloy for electric and electronic devices, comprising the steps of:

a) subjecting to hot working a copper alloy which comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt % of Zn, 0.005 to 0.1 wt% of Cr, and the balance Cu and the inevitable impurities;

b) cooling the alloy at a rate of over 15°C per second from a temperature exceeding 600°C ; and

c) after cold working, annealing the alloy at 400°C to 550°C for 5 minutes to 4 hours.

14

The present invention overcomes the disadvantage of ordinary Cu-Ni-Si alloys as substrates for tin and tin alloy platings which exhibit poor resistance to peeling, and is based on the findings to be

5 described. The invention provides copper alloys for electric and electronic devices which exhibit excellent resistance to peeling of the tin and tin alloy platings and also a method for producing such alloys.

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The copper alloys of the invention used in the manufacture of electric and electronic devices and the method for producing the alloys involve the following three embodiments:

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1) a first embodiment in which the copper alloy comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn and the balance Cu and the inevitable impurities: 2) a second
20 embodiment in which the copper alloy comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, 0.005 to 0.1 wt% of Cr and the balance Cu and the inevitable impurities; 3) third
25 embodiment which is directed to a method of producing copper alloys for electric and electronic devices which is characterised by subjecting, to hot working, a copper alloy comprising 3.0 to 3.5 wt% of Ni,

0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, with or without 0.005 to
30 0.1 wt% of Cr, and the balance Cu and the inevitable impurities, cooling the alloy from temperatures over 600°C at a rate of over 15°C per second, and, after cold working, annealing the worked product at 400°C to 550°C for 5 minutes to 4 hours.

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The composition of the inventive copper alloy is described in detail as follows:

Ni is an element which can impart strength to the alloy. If the Ni content of the alloy is less than 3.0 wt%, no improvement of strength can be expected even though Si is present within the range of 0.5 to 0.9 wt%. On the other hand, if the Ni content is over 3.5 wt%, no improved effect can be expected and there is a reduction in economy. Accordingly, the Ni content of the alloy is in the range of 3.0 to 3.5 wt%.

Si is an element which can improve the strength of the alloy similar to Ni. Amounts of the element less than 0.5 wt% do not improve its strength even though Ni is present in the range of 3.0 to 3.5 wt%. Amounts of Si exceeding 0.9 wt% are disadvantageous in that they decrease the conductivity of the alloy and also result in a deterioration of the hot workability of the alloy. Accordingly, the Si content should be within the range of 0.5 to 0.9 wt%.

Mn is an element which can improve the hot workability of the alloy. If its content is less than 0.02 wt%, this improvement is reduced. On the other hand, if the Mn content exceeds 1.0 wt%, the casting flowability deteriorates so that there is a considerable lowering of the casting yield. Accordingly, the content of Mn should be within the range of 0.02 to 1.0 wt%. In order not to suffer losses in electrical conductivity, however, the content of Mn should be within the preferred range of 0.02 to 1.0 wt%.

16

Zn is an element which can remarkably improve the resistance to peeling of the tin and tin alloy platings. If the content of Zn in the alloy is less than 0.1 wt%, this effect is reduced, whereas
5 if the content is larger than 5.0 wt%, the solderability of the alloy deteriorates. Accordingly, the content of Zn in the alloy should be within the range of 0.1 to 5.0 wt%.

10 Cr is an element which improves the resistance to peeling of tin and tin alloy platings similar to Zn. However, if Cr is used alone, the same effect as is achieved by the use of Zn alone cannot be attained. In other words, even though Zn is present in an
15 amount of 0.1 to 5.0 wt% in the alloy, its effect will be reduced if the content of Cr is less than 0.005 wt%. If, on the other hand, Cr is present above 0.1 wt%, the casting flowability of the alloy considerably deteriorates with an attendant deterioration
20 of casting yield. Accordingly, the content of Cr should be within the range of 0.005 to 0.1 wt%.

An embodiment of the method of preparation of the alloy is as follows.

25 A casting obtained by an ordinary ingot technique is subject to hot working, after which it is cooled from temperatures over 600°C at a cooling rate of 15°C per second. For temperatures less than 600°C
30 even though the cooling rate employed is over 15°C/second, precipitation hardening will already have taken place in the material, which worsens the cold workability of the alloy in a subsequent step. On the other hand, if the cooling rate is less than 15°C/
35 second, even though the starting temperature is over 600°C, precipitation hardening likewise occurs.

17

Accordingly, the quenching temperature should be over 600°C and the cooling rate should be over 15°C/second.

- 5 Annealing after cold working imparts the effect of imparting peeling resistance to the tin and tin alloy platings. It has been confirmed by X-ray analysis that peeling of tin or tin alloy coatings becomes considerable when there is only little
- 10 precipitation of Ni_2Si and when Ni and Si form a solid solution. With the copper alloys for electric and electronic devices according to the present invention, the temperature at which the greatest amount of Ni_2Si precipitates by annealing after cold
- 15 working, ie where the conductivity of the alloys becomes a maximum is 500°C. At temperatures less than 400°C, reduced amounts of Ni and Si compounds precipitate. These solid solutions of Ni and Si exert an adverse effect on resistance to peeling.
- 20 Accordingly, the annealing temperature should be within the range of 400°C to 440°C. If the annealing time is less than 5 minutes, precipitation is insufficient, whereas a time period of over 4 hours is uneconomic. Accordingly, the annealing temper-
- 25 ature should be within the range of 400°C to 550°C and the annealing time should be within the range of 5 minutes to 4 hours.

- Having generally described this invention, a further
- 30 understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

18

Table 1

Example		Chemical Components (wt%)					Remarks
No.	Ni	Si	Mn	Zn	Cr	Cu	
1	3.24	0.67	0.029	0.10	-	balance	Inventive alloy
5	2	3.28	0.69	0.038	0.21	-	balance "
	3	3.28	0.69	0.038	0.46	-	balance "
	4	3.28	0.68	0.040	0.20	0.05	balance "
	5	3.28	0.69	0.034	-	-	balance Comparative alloy
	6	3.26	0.68	0.038	0.05	-	balance "
10	7	3.28	0.68	0.023	5.06	-	balance "
	8	3.22	0.67	0.038	-	0.04	balance "

Ingots having the alloy components and contents indicated in Table 1 are produced by the following procedure.

Verypure Cu is melted in an electric furnace while covered with charcoal at a temperature of about 1200°C. About 20% of the Cu charge is left and Ni is charged into the alloy in such an amount that a predetermined content of Ni is attained. After melting, Si is charged and, if desired, Cr is further added as an intermediate alloy of Cu-10 wt% Cr. After these starting materials have been melted down, the

191

- 9 -

balance of the Cu is charged and the molten metal temperature is decreased to 1180°C to 1190°C, followed by the addition of Zn, and casting of the molten alloy into a mold to obtain, after surface milling, a 50 mm thick x 80 mm wide x 130 mm long ingot.

These ingots are heated to 850°C and hot worked to a thickness of 15 mm, followed by charging of the ingot into water from 700°C. At this time, the cooling rate is 30°C/second. Thereafter, the ingots are cold worked to a thickness of 0.5 mm, followed by annealing at 500°C for 2 hours for the subsequent soldering test.

15 PREPARATION OF SAMPLES

The annealed materials are each cut into pieces 0.5 mm thick x 25 mm wide x 50 mm long, and are polished with Scotch bright, and the polished pieces are subjected to electrolytic abrasion and soldering with tin alloy according to the MIL STD-202E method 208C. The soldered samples are subjected to the high temperature storage test.

25 The storage conditions involve heating under conditions of 150°C at 500 hrs in air. The samples are then evaluated for resistance to peeling by bending the soldered portion at 180°C and then bending the piece back to its original shape. The resistance to peeling of the alloy is then evaluated by stripping the tape stuck on the alloy.

In Table 2 the soldering properties of the alloys of the present invention are shown as well as the same properties of comparative alloys. In Table 3,

23

the results of peeling resistance tests after high temperature storage are shown.

TABLE 2

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SOLDERABILITY TEST

10	<u>Conditions</u>	<u>Sample No.</u>	<u>Solderability</u>	<u>Remarks</u>
	MIL-STD-202E Method	1	Good	Inventive alloy
	208C	2	Good	"
	Solder: 60Sn/40 PB	3	Good	"
15	Temperature: 230°C	4	Good	"
		5	Good	Comparative alloy
		6	Good	"
		7	Poor	"
20		8	Good	"

TABLE 3

HIGH TEMPERATURE STORAGE TEST

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	<u>Conditions</u>	<u>Sample no.</u>	<u>Peeling of Solder Plating</u>	<u>Remarks</u>
	150°C	1	No peeling	Inventive alloy
30	500 hrs	2	"	"
	Heating in	3	"	"
	Air	4	"	"
		5	Peeled	Comparative alloy
35		6	Parly peeled	"
		7	No peeling	"
		8	Partly peeled	"

As will become apparent from the results of Tables 2 and 3, the copper alloys according to the present invention exhibited good soldering properties and involve no peeling of solder. Thus, the alloys prove to be very reliable and are satisfactory for use in the manufacture of electric and electronic devices.

An embodiment of the present method for producing the copper alloys of the invention is described as follows along with comparative examples.

Copper alloy no. 2 shown in Table 1 is hot worked at 850°C from 50 mm to 15 mm and then quenched at 700°C. The cooling rate is 30°C/second. Thereafter, the alloy is cold worked to 0.5 mm and annealed at 375°C and at temperatures ranging from 400°C to 600°C at intervals of 50°C for 2 hours. It will be noted that short time annealing at 500°C for 3 minutes is effected and the annealed samples are subjected to the high temperature storage test. The preparation of samples, soldering and evaluation are carried out in the same manner as described before.

In Table 4, the peeling resistance of the solder prepared by the method of the present invention is shown with respect to an alloy of the same composition but prepared by the indicated comparative example.

TABLE 4

HIGH TEMPERATURE STORAGE TEST

5	Conditions	Annealing Temperature	Annealing Time	Peeling of Solder	Remarks
	150°C	450°C	2 hrs	No peeling	Method of invention
	500 hrs	500°C	2 hrs	"	"
10	Heating	550°C	2 hrs	"	"
	In Air	500°C	3 mins	Partly peeled	Comparative method
		375°C	2 hrs	Peeled	"
15		600°C	2 hrs	Partly peeled	"

As is apparent from Table 4, the method of the present invention can produce copper alloys as substrates for solder layers which do not peel, and thus the present alloys are highly reliable and satisfactory for use in the manufacture of electric and electronic devices. In order to obtain the intended mechanical strength after annealing, the method of the present invention may include, after cold working, tension annealing or AP line (continuous annealing and pickling line) for the purpose of correcting any strains.

It will be noted that plating or coating may be effected by any suitable technique such as an electro-chemical technique, dipping or vacuum deposition.

As will be appreciated from the foregoing, the copper alloys of the present invention and the method of preparation result in a product whose outstanding feature is that no peeling of tin and tin alloy platings 5 (solder platings) is involved and the alloys are very suitable when used for the manufacture of electric and electronic devices.

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CLAIMS

1. A copper alloy for electric and electronic devices comprising: 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn and the balance Cu and the inevitable impurities.

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2. A copper alloy for electric and electronic devices comprising: 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, 0.005 to 0.1 wt% of Cr, and the balance Cu and the
10 inevitable impurities.

3. A method for producing a copper alloy for electric and electronic devices, comprising the steps of:

15 a) subjecting to hot working a copper alloy which comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, and the balance of Cu and the inevitable impurities;

b) cooling the alloy at a rate of over 15°C per second
20 from a temperature exceeding 600°C; and

c) after cold working, annealing the alloy at 400°C to 550°C for 5 minutes to 4 hours.

4. A method for producing a copper alloy for electric
25 and electronic devices, comprising the steps of:

a) subjecting to hot working a copper alloy which comprises 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.02 to 1.0 wt% of Mn, 0.1 to 5.0 wt% of Zn, 0.005 to
30 0.1 wt% of Cr, and the balance Cu and the inevitable impurities.

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- 15 -

- b) cooling the alloy at a rate of over 15°C per second from a temperature exceeding 600°C ; and
- c) after cold working, annealing the alloy at 400°C to 550°C for 5 minutes to 4 hours.

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5. Copper alloys as claimed in claim 1 substantially as hereinbefore described.

6. A method for producing a copper alloy as claimed
10 in claim 3 substantially as hereinbefore described.
