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## COPPER ALLOYS FOR SPRINGS

Tsuneaki Mikawa, Tokyo, Japan, assignor to Nippon Kinzoki Co., Ltd., Tokyo, Japan, a corporation of Japan

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### ABSTRACT OF THE DISCLOSURE

A copper alloy for springs consisting essentially of from 0.01 to 10% nickel, from 0.001 to 5% cobalt, from 0.01 to 5% silicon, from 0.01 to 10% aluminum, from 0.1 to 3% titanium and the balance copper, said copper content being in the range of 75% to 95%, and a copper alloy for springs having above composition and further including from 0.01 to 1% tellurium or from 0.01 to 10% manganese.

This invention relates to copper base alloys for springs and more particularly to copper alloys for springs which can be manufactured at low cost and having superior characteristics.

Generally, copper alloys have been widely used for manufacturing various type of springs because of their non-magnetic and corrosion resistant properties, high electrical and thermal conductivity and good workability. Typical copper alloys are phosphorus bronze and nickel-silver alloys which belong to the work hardening type group, and beryllium-copper alloy, titanium-copper alloy and the like which belong to the precipitation hardening type group.

Although phosphorus bronze and nickel-silver alloy are relatively inexpensive, their characteristics fail to satisfy modern industrial requirements. On the other hand, beryllium-copper alloy is very expensive, toxic, and difficult to prepare. Moreover its characteristics are not uniform. Further, titanium-copper alloy requires vacuum melting, and has poor characteristics, especially as to electrical conductivity.

An object of this invention is to provide a novel copper alloy of the precipitation hardening type having superior electrical conductivity and spring characteristics as compared with phosphorus bronze and nickel silver, but incorporating characteristics comparable with those of beryllium-copper and producible at a substantially lower cost.

Another object of this invention is to provide copper alloy for springs embodying excellent strength, heat resistance, wear resistance, fatigue resistance, electrical and thermal properties.

The copper alloy of this invention is characterized by incorporating predetermined amounts of Ni, Co, Si and Ti to the base consisting of aluminum bronze, thereby improving the mechanical property of the alloy without affecting its electrical conductivity and workability.

Copper, the basic metal of the alloy, embodies various inherent properties, which make it especially advantageous as an alloying material, such as excellent workability, high ductivity, excellent weldability, high corrosion resistance, adaptabilities to electroplating, paint coating, varnish coating, and easiness of insulation in addition to its high electrical conductivity. The copper alloy of this invention is based upon a unique utilization of these excellent physical, chemical and mechanical characteristics. The composition of the copper component of the alloy is in a range from 95 to 75%. Where the content of copper exceeds 95%, the characteristics of the copper alloy vary substantially whereas when the content is decreased below 75%, the

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above mentioned desirable characteristics of the copper alloy are reduced substantially.

The purpose of incorporating nickel is to promote the precipitation hardening property of the alloy thus improving the mechanical as well as the corrosion resistance properties the desirable content of nickel being from 10 to 0.01%. Incorporation of more than 10% nickel results in a decrease in the electrical conductivity, whereas incorporation of less than 0.01% is ineffective.

Incorporation of a proper quantity of cobalt results in a finer structure of the alloy thereby improving its workability and spring characteristic. The quantity of cobalt contained in the alloy ranges from 5 to 0.001%. A cobalt content of more than 5% is injurious, thus not only greatly affecting the workability and electrical conductivity but also increasing the cost of the alloy, whereas incorporation of cobalt of less than 0.001% produces no desirable effect.

Silicon contributes towards precipitation hardening without any appreciable decrease in electrical conductivity and also greatly improves the mechanical properties, especially the spring characteristics of the alloy. Further, silicon has an effect of deoxidation whereby to form sound ingots. The silicon content of the alloy preferably ranges from 5 to 0.01%. Addition of silicon of more than 5% reduces workability whereas addition of less than 0.01% is not effective.

The purpose of aluminum is to impart to the alloy corrosion resistance and age-hardening properties thus providing strength comparable to mild steel. Aluminum also functions as a deoxidizer to remove the deleterious effect of oxygen contained in the molten alloy ranges from 10 to 0.01%. Incorporation of aluminum in excess of 10% renders the alloy difficult to work, and incorporation of less than 0.01% produces no advantage.

Titanium promotes further the precipitation hardening characteristic afforded by Ni, Co and Si thus improving the mechanical properties, especially the spring characteristic of the alloy. Titanium content of the alloy is from 3 to 0.01%. Addition of titanium in excess of 3% impairs workability as well as electrical conductivity whereas addition of less than 0.01% is not effective.

To prepare a bland alloy suitable for use in various applications from a raw material having a composition described above, an ingot prepared by casting the molten raw material is first forged, and then hot and cold rolled to obtain a thin sheet of the alloy. The sheet is then heated to a temperature between 900° C. and 950° C. for effecting a solution heat treatment, maintained at this temperature for a predetermined time and immediately thrown in cold water to quench to obtain a homogenous solid solution. It was found that protracted solution heat treatment has resulted in coarse crystalline grains so that the desired property was not exhibited after precipitation hardening. Solution heat treatment time of from 7 to 30 minutes was found suitable for a sheet of a thickness of less than 2.5 mm. The solution heat treated material is then, or after being subjected to cold rolling (at a reduction rate of about 10 to 90%) for the purpose of strengthening it, subjected to an age hardening treatment at a temperature of from 400 to 550° C. The  $\alpha$  solid solution obtained by said solution heat treatment is an alloy supersaturated with components capable of precipitation hardening so that upon heating to an elevated temperature intermetallic compounds such as Al-Ni, Al-Co, Ni-Si and Cu-Ti<sub>3</sub> will be precipitated from the  $\alpha$  solid solution phase, thus greatly increasing the hardness of the alloy.

This invention also contemplates the incorporation of tellurium in the alloy to further improve the hot and cold workabilities of the alloy without appreciably impairing the inherent characteristics thereof. Addition of tellurium also improves the corrosion resistant property of

the alloy. Preferable range of tellurium content is from 1 to 0.01%.

When a certain amount of manganese is incorporated into the copper alloy of this invention, the electrical resistance is substantially increased rendering the alloy useable as a resistant material. Preferable range of manganese was found to be from 10 to 0.01%. As a deoxidizer, in addition to silicon, zirconium or tantalum may be utilized.

The copper alloy of this invention can be manufactured at a cost far lower than that of copper-beryllium, copper-titanium and like alloys which are known to have excellent characteristics. Moreover this novel copper alloy has excellent physical, mechanical and chemical characteristics so that it can be advantageously used in many applications. More particularly, it has a high hardness comparable to steel plus excellent spring characteristics. Further, as the alloy has a higher age hardening treatment temperature than beryllium-copper, its high temperature strength is higher than that of beryllium-copper thus exhibiting antiwearing property of the same degree as those of phosphorus bronze, copper-beryllium alloy and copper-titanium alloy. Moreover the corrosion resistance of the alloy against acids such as sulfuric acid, hydrochloric acid, acetic acid and the like is more than ten times higher than that of phosphorus bronze. Also corrosion resistance of the alloy against common salt, caustic soda and like basic agents is higher than that of phosphorus bronze. Consequently the alloy is suitable for use as spring material for electric machines and devices, electrical communication apparatus and measuring instruments, components of precision machines, spring material for ve-

hicles, and contact spring for automatic selling machines and the like. Moreover since the alloy has superior antiwearing and heat conductive characteristics it is suitable for use in machine parts which are required to have these characteristics. The alloy incorporated with manganese is a good electric resistance material so that it can be used for manufacturing thermo-couples and other similar elements.

The following specific examples are given by way of illustration, and are not to be construed as limiting in any way the scope and spirit of the invention. All parts are by weight.

#### EXAMPLE 1

A raw material consisting of 84.22% of copper, 2.91% of cobalt, 6.65% of nickel, 0.98% of silicon, 4.72% of aluminum, and 0.52% of titanium was melted at a temperature of from 1010 to 1200° C., borax was incorporated into the molten metal for deoxidization and the molten metal was poured into a mold. After forging, the ingot obtained was successively subjected to hot and cold rolling operations, solution heat treatment, cold rolling operation and an age hardening treatment in a manner described above to provide a sample sheet of about 0.3 mm. thick. The following Table I shows the test results of various chemical characteristics of the sample sheet after immersion in the solutions of noted reagents maintained at 37° C. for 72 hours respectively. For comparison, similar results of copper-beryllium are shown in Table II. The test results of the physical characteristics of the sample sheet are shown in Table III, and Table IV shows the comparison between physical characteristics of the alloy of this invention and of various prior alloys.

TABLE I.—CHEMICAL TEST OF THIS ALLOY  
[Partial dipping test at 37° C. for 72 hours]

| Solution               | Concentration                   |                                 |                                 |                                 |
|------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|                        | 0.5%                            | 1%                              | 2%                              | 5%                              |
| Hydrochloric acid..... | No weight loss, no discoloring. | No weight loss, no discoloring. | No weight loss, no discoloring. | No weight loss, no discoloring. |
| Common salt.....       | do.                             | do.                             | do.                             | Do.                             |
| Sodium sulfide.....    | do.                             | do.                             | do.                             | Do.                             |
| Lactic acid.....       | do.                             | do.                             | do.                             | Do.                             |

TABLE II.—CHEMICAL TEST OF OTHER ALLOYS  
[Partial dipping test at 37° C. for 72 hours]

| Solution               | Concentration                        |                                    |                                    |                                   |
|------------------------|--------------------------------------|------------------------------------|------------------------------------|-----------------------------------|
|                        | 0.5%                                 | 1%                                 | 2%                                 | 5%                                |
| Hydrochloric acid..... | No weight loss, slightly discolored. | Weight loss, 0.081 mg. discolored. | Weight loss, 0.012 mg. discolored. | Weight loss, 0.16 mg. discolored. |
| Common salt.....       | do.                                  | Slight weight loss, discolored.    | Weight loss, 0.004 mg. discolored. | Weight loss, 0.06 mg. discolored. |
| Sodium sulfide.....    | do.                                  | do.                                | Slight weight loss, discolored.    | Slight weight loss, discolored.   |
| Lactic acid.....       | do.                                  | do.                                | do.                                | Do.                               |

TABLE III.—PHYSICAL TEST OF THIS ALLOY

| Conditions of materials                                                 | Test items                               |                      |               |                                                    |                                        |
|-------------------------------------------------------------------------|------------------------------------------|----------------------|---------------|----------------------------------------------------|----------------------------------------|
|                                                                         | Tensile strength (kg./mm. <sup>2</sup> ) | Elongation (Percent) | Hardness (HV) | Spring critical value (kg./mm. <sup>2</sup> ) (Kb) | Electrical Conductivity (IACS percent) |
| After solution treatment and tempering at 525° C., 1 hr.....            | 83.4                                     | 34.2                 | 165           | 71.3                                               | 14.28                                  |
| After cold rolling of 23% reduction and tempering at 500° C., 1 hr..... | 98.2                                     | 11.5                 | 320           | 86.5                                               | 13.95                                  |
| After cold rolling of 50% reduction and tempering at 425° C., 1 hr..... | 115.0                                    | 2.5                  | 358           | 110                                                | 12.47                                  |

TABLE IV.—PHYSICAL TEST OF VARIOUS ALLOYS

|                           | Test items                               |                      |               |                                         |                                               |                                                    |
|---------------------------|------------------------------------------|----------------------|---------------|-----------------------------------------|-----------------------------------------------|----------------------------------------------------|
|                           | Tensile strength (kg./mm. <sup>2</sup> ) | Elongation (Percent) | Hardness (HV) | Electrical conductivity (LA CS percent) | Modulus of elasticity (kg./mm. <sup>2</sup> ) | Spring critical value (kg./mm. <sup>2</sup> ) (Kb) |
| This alloy.....           | 180-116                                  | 1-10                 | 340-370       | 10-30                                   | 12,000                                        | 80-110                                             |
| Copper beryllium.....     | 105-151                                  | 1-10                 | 327-447       | 22-25                                   | 12,500                                        | 100-110                                            |
| 8% phosphorus bronze..... | 42, 1-78, 5                              | 3-65                 | 93-240        | 13                                      | 11,000                                        | 60-70                                              |
| 6/4 Brass.....            | 37, 9-49, 2                              | 10-45                | 82-138        | 28                                      |                                               |                                                    |
| 65/18 Nickel silver.....  | 40, 7-59, 8                              | 3-40                 | 82-170        | 6                                       | 14,000                                        | 60-70                                              |
| 8% Aluminum bronze.....   | 45, 7-73, 8                              | 7-60                 | 92, 5-226     | 14.8                                    |                                               |                                                    |

EXAMPLE 2

The same sample as in Example 1 was prepared except for the addition of 0.05% of tellurium and similar characteristics were obtained. The alloy of this example showed reduced reject of products after hot and cold working.

EXAMPLE 3

An alloy consisting of 80% of copper, 3% of nickel, 3% of cobalt, 0.5% of zirconium, 5% of aluminum, 0.5% of titanium and 8% of manganese was prepared and tested regarding physical and chemical characteristics thereof by the same method as described in connection with Example 1. The test results were the same as those of Example 1 excepting electric resistance characteristics shown in Table V below.

TABLE V.—TEST OF ELECTRICAL RESISTANCE

| Samples              | Test items          |                 |                 |                                                |                        |                                     |
|----------------------|---------------------|-----------------|-----------------|------------------------------------------------|------------------------|-------------------------------------|
|                      | Specific resistance |                 |                 | Temperature coefficient of specific resistance |                        | Electric Conductivity (at 30.5° C.) |
|                      | 30.5° C.            | 6° C.           | 5.5° C.         | 6° C.-35.5° C.                                 | 5.5° C.-35.5° C.       |                                     |
| A <sup>1</sup> ..... | 49.086μ ohm-cm.     | 49.047μ ohm-cm. |                 | 3.245×10 <sup>-3</sup>                         |                        |                                     |
| B <sup>2</sup> ..... | 49.540μ ohm-cm.     |                 | 49.514μ ohm-cm. |                                                | 2.100×10 <sup>-3</sup> |                                     |
| Mean value.....      | 49.31μ ohm-cm.      |                 |                 | 2.67×10 <sup>-3</sup>                          |                        | 2.027×10 <sup>8</sup> Ω/m.          |

<sup>1</sup> As rolled.    <sup>2</sup> After aging treatment.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A copper alloy for springs consisting essentially of from about 0.01% to about 10% nickel, from about 0.001% to about 5% cobalt, from about 0.01% to about 5% silicon, from about 0.01% to about 10% aluminum, from about 0.01% to about 3% titanium and the balance copper, said copper content being in the range of about 75% to about 95%.

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CHARLES N. LOVELL, Primary Examiner.