United States Patent [19]

Mikawa

[11] **3,901,692**

[45] **Aug. 26, 1975**

[54] **CORROSION RESISTANT COPPER ALLOY AND THE METHOD OF FORMING THE ALLOY**

[76] Inventor: **Tsuneaki Mikawa,** 11, 1-Chome, Nakadai-cho, Itabashi, Tokyo, Japan

[22] Filed: **Mar. 15, 1973**

[21] Appl. No.: **341,685**

Related U.S. Application Data

[63] Continuation of Ser. No. 171,354, Aug. 12, 1971, abandoned, which is a continuation-in-part of Ser. No. 67,999, Aug. 28, 1970, abandoned.

[30] **Foreign Application Priority Data**

Aug. 29, 1969 Japan 44-67930

[52] **U.S. Cl.** **75/159;** 75/153

[51] **Int. Cl.** **C22c 9/06**

[58] **Field of Search** 75/153, 159, 161, 162; 148/32, 32.5

[56] **References Cited**

UNITED STATES PATENTS

1,718,502	6/1929	Vaders	75/162 X
2,195,433	4/1940	Silliman	75/153
2,430,419	11/1947	Edens	75/159
2,715,577	8/1955	Payne et al.	75/162
2,798,826	7/1957	Klement	75/159
2,870,051	1/1959	Klement	75/162 X
3,297,437	1/1967	Bosman	75/161 X
3,364,016	1/1968	Mikawa	75/159
3,416,915	12/1968	Mikawa	75/159

FOREIGN PATENTS OR APPLICATIONS

229,683	7/1960	Australia	75/159

Primary Examiner—C. Lovell

Attorney, Agent, or Firm—Armstrong, Nikaido & Wegner

[57] **ABSTRACT**

A corrosion resistant copper alloy having copper as its principal component and in addition containing 0.1 to 11 percent aluminum, 0.1 to 10 percent nickel, 0.001 to 1.0 percent boron, 0.01 to 6 percent iron, 0.01 to 10 percent manganese and, optionally, 0.01 to 5 percent cobalt. Also, a method for making the alloy in which manganese is added to a melt containing nickel, boron, iron, and copper in order to eliminate any gaseous oxygen, following which step the aluminum can be added.

4 Claims, No Drawings

CORROSION RESISTANT COPPER ALLOY AND THE METHOD OF FORMING THE ALLOY

This is a continuation, of application Ser. No. 171,354, filed Aug. 12, 1971, now abandoned; which is in turn a continuation-in-part of application Ser. No. 67,999 filed Aug. 28, 1970 and now abandoned.

BACKGROUND OF THE INVENTION

It is well known that copper is one of the most excellent metallic materials because of its high heat and electrical conductivity properties. However, where carbon dioxide gas exists, a change of color takes place and the copper will become green. A further weak characteristic of copper is that it is likely to be damaged by aqueous salt containing solutions and by ammonium salts.

It is an object of this invention to develop an alloy having the good qualities of copper, namely, the ability to conduct electricity and heat, while concomitantly reinforcing the corrosion resistant nature and the acid resistant nature of the metal; lowering the melting point of the alloy, and enhancing its manufacturability.

SUMMARY OF THE INVENTION

This invention relates to a corrosion resistant copper alloy that is comprised of copper as its principal component. In addition, the alloy contains specific amounts of aluminum, nickel, boron, iron, and manganese. A small quantity of cobalt can also advantageously be added. It is also important that the method of producing the alloy, as described hereinbelow, be followed. The resulting copper alloy is highly suitable and desirable for use in the industrial arts and manufacturing industries.

DETAILED DESCRIPTION OF THE INVENTION

In my earlier U.S. Pat. No. 3,416,915 I have described a similar copper alloy which also has many desirable properties. The present alloy, however, differs from that described in my earlier patent in that the workability of the alloy of this application is greatly improved. The present alloy is highly ductile and, therefore, it can be drawn into wire. In addition, its improved workability allows the formation of powders, sheets and high quality springs. The alloy is also suitable for high voltage electrical contacts. A further advantage of the present alloy over that of my earlier patent is that the corrosion resistance is improved. All of these advantages of the present alloy can be traced to the use of manganese and, in the preferred embodiment, the addition of cobalt; and also to the sequence of steps used in forming the alloy during which process the manganese is added to deoxidize the molten mass and thereafter the aluminum is added.

In accordance with the present invention there is provided a copper alloy that is comprised of 0.1 to 11 percent aluminum, 0.1 to 10 percent nickel, 0.001 to 1.0 percent boron, 0.01 to 6 percent iron, 0.01 to 10 percent manganese, and the remainder substantially all copper. In one embodiment of the invention, cobalt can be added in an amount of from 0.01 to 5 percent according to its necessity. Throughout the specification and claims all percents refer to percent by weight unless otherwise stated.

It is important that the mixing ratios of the component metals of the alloy be limited to the disclosed ranges for the reasons set forth hereinbelow.

Nickel is added to further reinforce the corrosion resistance of the alloy as well as to improve its heat resisting nature and its mechanical quality. It is important, however, that no more than 10 percent of nickel be added because amounts in excess of 10 percent will bring about a decrease in the capability of being manufactured. In addition, the use of less than 0.1 percent of nickel will be inadequate to achieve its expected purpose and quality. Therefore, the amount of nickel should be between about 0.1 percent and 10 percent. According to a preferred embodiment, nickel is present in an amount of about 5–7 percent.

Boron is added to eliminate the damage caused by impurities. It operates by neutralizing the hardening nature and impurities of the copper alloy. The boron also aids in deoxidizing the copper, and in improving the heat resistant and corrosion resistant properties of the copper alloy. However, when more than 1 percent of boron is added, it adversely affects the manufacturability of the alloy. An infinitesimal amount of boron, below 0.001 percent, will not be adequate to improve the properties of the alloy. Therefore, in order to attain the expected purpose and quality of the copper alloy, the mixing ratio of boron should be between about 0.001 percent and 1.0 percent, preferably between about 0.08 and 0.5 percent.

Iron is added in order to improve the workability of the alloy as well as to reinforce the heat resisting and corrosion resisting nature thereof. However, if more than 6 percent iron is used, it will result in an undesirable increase of the point of fusion of the alloy, and in addition, the workability as well as the processability of the copper alloy will become impaired. When less than 0.01 percent of iron is used, it will not result in the expected quality, and the copper alloy will not be capable of use in various desirable ways. Therefore, the mixing ratio of iron should be between about 0.01 percent and 6 percent, and preferably between about 3 to 4 percent. Carbon may optionally be present in the iron utilized in the alloy of the invention. It is preferrable that the carbon content of the iron be low, generally not in excess of 0.0002 percent of the iron.

It is essential that, in the course of making the alloy, manganese be added to the molten solution to form manganese oxide. This stabilizes the oxygen in the molten solution and acts as a deoxidizer in order to prevent the bad operation and deleterious effects caused by gaseous oxygen.

According to a first embodiment of the invention, it is preferred that not greater than 5 percent manganese be used, due to the ease of manufacture of the alloy. At least 0.01 percent manganese should be present in order to accomplish the desired deoxidation effect. The mixing ratio of the manganese according to this first aspect of the invention is therefore between about 0.01 percent and 5 percent.

According to a second embodiment of the invention, it is preferred that manganese be used in an amount of from about 5 percent to 10 percent, in order to provide an alloy of excellent characteristics for use in springs and other materials where elasticity is an important property. Although less than 5 percent manganese may be used, it has been found that at least 5 percent manganese provides superior results. A maximum of 10 percent manganese is preferred due to undesirable characteristics of the alloy with higher amounts of manganese, such as cracking of the alloy. Preferably, the

manganese content is from about 7 to about 9 percent. Optimum results have been obtained where the manganese content is 8 percent.

Aluminum is excellent in its corrosion resisting nature and in its capability of being formed and manufactured at the beginning stage, and also it is high in the conduction of heat and electricity. By taking advantage of these characteristics, the corrosion resisting nature of the copper alloy can be reinforced and the alloy can also be made harder and more durable. In addition, the alloy will retain its strength to a degree equal to soft steel. Furthermore, the aluminum improves the color of the alloy giving it a golden appearance. However, when more than 11 percent of aluminum is added, the manufacturability is reduced, and if the amount falls below 0.1 percent, the corrosion resisting nature becomes worse. Therefore, the amount of aluminum is set between about 0.1 percent and 11 percent, and preferably between about 6 and 7 percent. It has also been discovered that during processing, the aluminum should be added after the hot melt has been deoxidized. By conforming to such sequence the properties of the product are greatly improved.

In addition to the hereinabove described metals which comprise the alloy of the invention, cobalt can be added as an optional ingredient. The cobalt improves the malleability of the alloy as well as imparting corrosion resistance, friction resistance, and heat resistance thereto. Moreover, cobalt will aid in allowing the production of a powdered alloy having very fine and delicate grains and will also help the alloy gain elasticity which is very useful where the alloy is to be used for making springs. However, when more than 5 percent of this cobalt is added, it causes a reduction of elasticity, and if the amount of cobalt is below 0.01 percent, it will not bring about the desired results and effects. Therefore, when cobalt is present, it is desirable to use an amount of cobalt between about 0.01 and 5 percent. It has been found that cobalt is a particularly advantageous ingredient in the alloy of the invention when the alloy is used for the manufacture of springs and other materials where elasticity is an important property.

The main part of the alloy is, of course, composed of cooper which constitutes the remainder of the alloy other than the foregoing materials. The copper contributes the dominating characteristics of the copper alloy, and the many improved characteristics imparted by the additional materials described hercinabove result in the formation of a copper alloy that is excellent in all of those qualities, the most striking of which are its corrosion resisting nature and its manufacturability.

It is preferrable that the materials used in the preparation of the alloy of the invention be free from impurities, particularly impurities such as lead, tin, zinc and silicon. It has been found that even minor quantities of such impurities provide an alloy with inferior characteristics, particularly corrosion resistance. In order to avoid this problem, impurities in the metals used should be minimal, and should be kept below 0.001 percent of the weight of the alloy.

The following examples illustrate this invention in detail.

EXAMPLE I

The following elements are mixed as solids and then treated at 1450°C to form a solution:

Nickel	2.5%
boron	0.2%
iron	3.0%

To the above solution there is added 88.1% copper and the heating is continued for 2 hours to insure that the metals are thoroughly melted. Thereafter, there is added 0.2 percent manganese for the purpose of deoxidation. Finally, 6 percent aluminum is then added to the mixture to form the alloy of the invention. The molten mass is then cooled. The melting point of the copper alloy thus produced is about 1250°C.

EXAMPLE II

An alloy was made in accordance with the procedure described in Example I except that the amount of nickel was increased to 6.5% and 3% of cobalt is added to the hot melt of copper, nickel, iron and boron, in order to reinforce the elasticity. The amount of copper was reduced to 81.1% to compensate for the increase in nickel content and for the addition of cobalt. After this operation, the same process as explained in Example I above can be performed, namely, the addition of manganese and then aluminum. The addition of cobalt enhances the properties of the alloy and makes it especially useful for high quality springs.

Copper alloys produced in the manner described herein of the foregoing components have a beautiful, golden-bright, metallic, lustrous appearance, and are also sulfur resistant and highly corrosion resistant. The melting point is about 1250°C, and can easily be melted down and fabricated mechanically. Therefore, these copper alloys are excellent for use for ornamentation and industrial arts, miscellaneous goods, architectural materials, parts and accessories of electrical appliances and automobiles, and the like.

EXAMPLE III

When 5.0 percent manganese is substituted for the 0.2 percent manganese of Example I, an excellent product of similar properties is produced.

EXAMPLE IV

When 8.0% manganese is substituted for the 0.2 percent manganese of Example I, an excellent product of improved elastic properties is produced.

EXAMPLE V

When 8.0% manganese is substituted for the 0.2 percent manganese of Example II, a product of excellent elastic properties is produced.

EXAMPLE VI

The following are the results derived from chemical experiments on the copper alloy described herein.

1. The copper alloy of Example I was soaked in solutions of strengths of from 0,5 to 5 percent (0.5 –5%) of sodium chloride, sodium sulphide, and lactic acid for three (3) days, at a temperature of 37°C, but neither a decrease in weight nor any change of color developed in any of these solutions.

2. The copper alloy of Example I was soaked in hydrochloric acid solution for three (3) days, at a temperature of 37°C. With hydrochloric acid of 5 percent concentration, no decrease in weight or change of color took place. With concentrations of from 1 percent up

to 5 percent, the color changed only slightly and there was no change in weight.

The results of physical experiments on the copper alloy of Example I are as follows: tensile strength, 90 – 110 (Kg/mm²); elasticity, 10 – 25(%); hardness, 150-230 (Brinell HV); specific gravity, 8.8. This indicates that the tensile strength, elasticity, and hardness are even greater than the commonly used Cactus Gold and Atomic Gold, and the specific gravity (8.8) is greater than that of Cactus Gold (7.8) and Atomic Gold (8.0).

A sample of the cobalt containing spring alloy of Example II was compared to a conventional Copper-Beryllium alloy which also contained cobalt.

Results of Comparative Tests of an Alloy[1] of this Invention with a Copper-Beryllium Alloy

	Tensile Strength Kg/mm²	Elongation %	Brinell Hardness HV	Electrical Conductivity LACS %	Modulus of Elasticity Kg/mm²	Spring Critical Value Kg/mm²Kb
Alloy of Invention	180–116	1–10	340–370	15–20	12,000	80–110
Cu-BeAlloy	105–151	1–10	327–447	22–25	12,000	100–110

[1]Alloy of Example II

In view of the many excellent properties exhibited by the alloy of the invention, it is suited for a wide variety if uses. The alloy of the invention has been found to provide springs of excellent elastic characteristics. In addition to the use of the alloy of the invention in springs, due to the excellent corrosion resistance and strength of the alloy and its pleasing physical appearance, it may also be used for the manufacture of watch cases and bands, costume jewelry, golf club heads, ship fittings such as railings and screws, drawer handles and tableware. In addition, the alloy of the invention has been proposed for use in machinery parts and as a structural material for buildings in place of bronze materials used heretofore.

What is claimed is:

1. A copper alloy having excellent corrosion resistance consisting essentially of, by weight:
6 to 7% aluminum
5 to 7% nickel
0.08 to 0.5% boron
3 to 4% iron
5 to 10% manganese
with remainder being essentially copper containing less than 0.001% impurities.

2. A copper alloy of claim **1** and further including between about 0.01 and 5 percent of cobalt.

3. A copper alloy of claim **1,** wherein manganese is present in an amount of from 7 to 9 percent.

4. A copper alloy of claim **3,** wherein manganese is present in an amount of about 8 percent.

* * * * *