United States Patent [19]

Watanabe et al.

[11] **3,830,644**

[45] **Aug. 20, 1974**

[54] **COPPER ALLOY FOR PLASTIC-WORKING MOLDS**

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[73] Assignee: **Hitachi Shipbuilding and Engineering Co., Ltd.**, Osaka City, Japan

[22] Filed: **Apr. 3, 1972**

[21] Appl. No.: **240,571**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 859,341, Sept. 19, 1969, abandoned.

[52] **U.S. Cl.** **75/153**, 75/154, 75/157.5, 75/162

[51] **Int. Cl.** **C22c 9/10**

[58] **Field of Search** 75/153, 157.5, 160, 154, 75/156, 156.5, 157, 157.5, 162; 148/32

[56] **References Cited**

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Primary Examiner—Charles N. Lovell
Attorney, Agent, or Firm—Tab T. Thein

[57] **ABSTRACT**

Copper alloy for plastic-working molds, containing as other principal components aluminum, beryllium, silicon and cobalt, having a value of 9 to 18 weight percent, calculated by an aluminum conversion formula Al + 1.8 percent Be + 1.5 percent Si and 1.5 percent Co, all in weight percent, and containing 6 to 15 percent Al, 0.6 to 2 percent Be, 0.9 to 3.5 percent Si, 0.5 to 2.5 percent Co and the balance Cu, the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, as well as high toughness and other desirable mechanical properties. In some cases, the alloy may additionally contain as secondary elements at least one of the elements Sn, Zn, Mn, Fe and Zr. The alloys are particularly suitable for dies in deep drawing, which are required to have high mechanical strength and wear resistance.

6 Claims, 4 Drawing Figures

FIG. 1

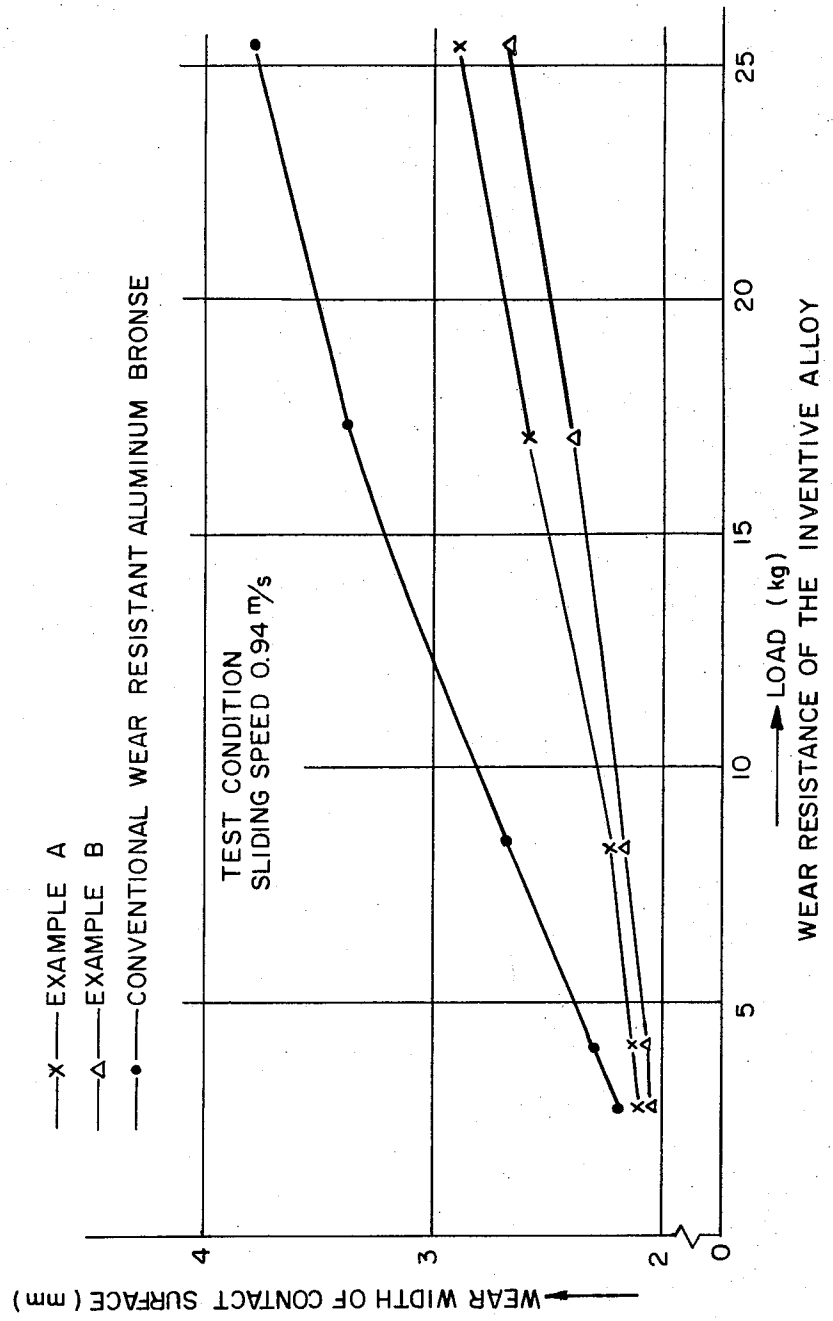

—X— EXAMPLE A
—△— EXAMPLE B
—●— CONVENTIONAL WEAR RESISTANT ALUMINUM BRONSE
TEST CONDITION
SLIDING SPEED 0.94 m/s
WEAR WIDTH OF CONTACT SURFACE (mm)
WEAR RESISTANCE OF THE INVENTIVE ALLOY
LOAD (kg)
0
5
10
15
20
25
2
3
4

FIG. 2

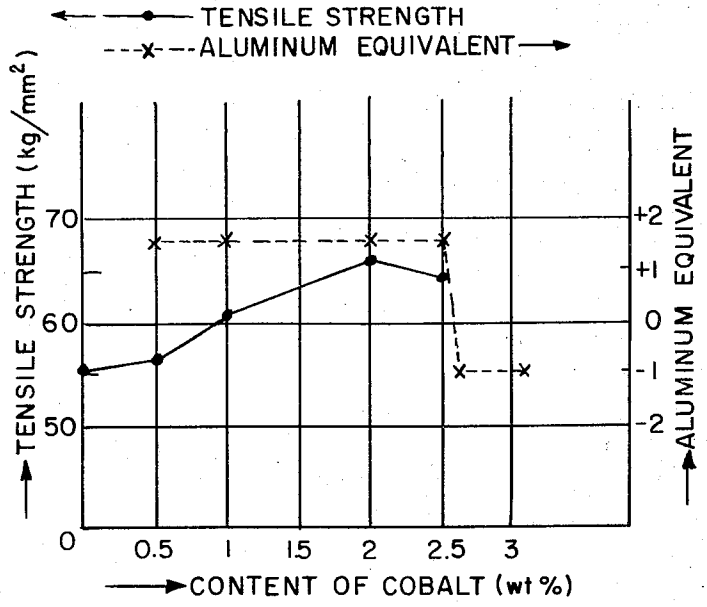


FIG. 3

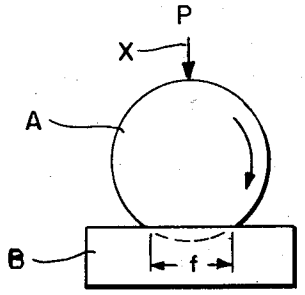
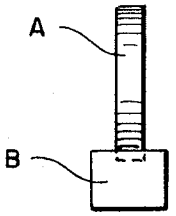


FIG. 4



COPPER ALLOY FOR PLASTIC-WORKING MOLDS

This is a continuation-in-part application of application Ser. No. 859,341, filed Sept. 19, 1969, now abandoned, which was titled "Copper Base Alloys".

There are a number of hyper-eutectoid copper-aluminum base alloys (aluminum bronze) which have been developed and proposed as wear-resistant materials.

In some of them a small amount of iron is added to improve the hardness, and in others a small amount of nickel, manganese, vanadium, etc. is added to improve other mechanical properties.

The present invention relates to a highly wear-resistant aluminum bronze of the precipitation-hardening type which, unlike the above-mentioned conventional aluminum-bronze materials, is prepared by adding aluminum to the copper base and a small amount of beryllium, silicon and cobalt, as more fully described hereinbelow.

The alloy of the present invention is further characterized in that the aluminum content can be decreased to a relatively low value in the hypo-eutectoid region without sacrificing the excellent wear resistance, therby achieving relatively high elongation.

Adding cobalt to Cu-Be alloys is already known, but from the metallurgical point of view, the cobalt addition in the alloy of the present invention is completely different from that in case of Cu-Be alloys as formerly employed. For further explanation of the metallurgical details, it may be mentioned that Cu-Be alloys are of aging type in which the added cobalt is effective in regulating the boundary precipitation of Be in the aging process. However, in the as-cast state this effect of Co-addition is never noticeable for the Cu-Be alloys.

Contrary thereto, the alloy according to the present invention is characterized in that it can be practically used in the as-cast state, such as for plastic-working molds, and in this respect it is an improvement over the conventional high-hardness copper base alloys which are necessarily heat-treated before practical use. The Co-addition in the alloy of the present invention relates to the precipitation behavior of the (Cu-Al) γ_2-phase and does not relate to the precipitation behavior of Be. Therefore the Co-addition in the present invention must be considered to be completely novel as regards metallurgical conditions.

Moreover, it is a discovery first made by the inventors that, with reference to the precipitation of the γ_2-phase, the Al-equivalent values of Be, Si and Co are about 1.8, about 1.5 and about 1.5, respectively. It is true that in Cu-Al binary alloys the precipitation of γ_2 is obtainable, without adding Be, Si and Co, merely by regulating the quantity of Al but such Cu-Al binary alloys, without any additional elements, cannot be used for practical purposes due to their coarse γ_2-phases as

well as their weakened eutectoid structures. In order to utilize the γ_2-phase, it is necessary to refine and nodulate the γ_2-phase and to regulate the eutectoid transformation.

These effects are obtainable by the aid of the above-mentioned Be, Si and Co addition. As a result of a series of our experiments concerning the wear resistance of Cu-Al alloys, it has been clarified that such a metallurgical structure as [50 to 70 percent fine nodular γ + balance β + acicular α + eutectoid ($\alpha+\gamma$)] is most outstanding. On the other hand, in CU-Al binary alloys, the balance metallurgical structure, which is obtained by such an Al-quantity as will precipitate a 50 to 70 percent γ structure, is a coarse ($\alpha+\gamma$) structure which cannot be practically utilized.

The alloy of the present invention is characterized in that the additional elements are added so as to change their metallurgical structures from a structure as [coarse γ + coarse ($\alpha+\gamma$)] to said excellent structure consisting of [50 to 70 percent fine nodular γ + balance β + acicular α + eutectoid ($\alpha+\gamma$)] in the as-cast state. Consequently, the alloy of the present invention is further characterized in that the γ-phase can be utilized even in a case when Cu-Al binary alloys have hypo-eutectoid compositions.

As to the effect of each of the additional elements, the following explanation will further contribute to a clearer understanding.

Beryllium is added to regulate a transformation speed of the eutectoid ($\alpha+\gamma$) phase, to leave a portion of the β-phase, and to aciculate an α-phase.

Co and Si are added in order to refine and to nodulate a coarse γ-phase. The simultaneous addition of Co and Si is intended for their mutual intensifying effect. Moreover, Co-addition strengthens the α-phase and the β-phase.

The following list shows the change of nodulated rates due to the addition of Co or Si alone, or both Co and Si together.

	Content Weight %						
	Cu	Al	Be	Si	Co	Nodulated rate of γ-phase (%)	Al equivalent (%)
A	87.8	9	0.8	—	2.4	about 43	about 14
B	88.3	7.6	0.8	3.3	—	about 35	about 14
C	87.91	8.2	0.79	2.3	0.8	about 95	about 14.3

Note: Nodulated Rate = completely nodulated γ-phase/total amount of precipitated γ-phase

As seen from the above, the combined use of Si and Co leads to a far better result in the nodulated rate of the γ-phase.

Copper base alloys containing as additives Be and Co are disclosed in U.S. Pat. No. 3,201,234, dated Aug. 17, 1965, to P. J. Scherbner et al., titled "Alloy and Method of Producing the Same". However the alloys described in the patent differ essentially from that of the present invention. In the alloys of the patent, titanium is a further additive of prime importance. The range of Ti present in the alloys is 0.02 to 0.2 and Co is in the range of 0.1 to 5 percent, that is, in an amount effective to react with the titanium to form at least one of the compounds TiCo, Ti_2Co and $TiCo_2$.

As explained in the patent the intermetallic compounds are present as nuclei of the grains of the alloy and the grain structure thus resulting is of materially greater fineness. Contrary to the addition of Ti and the

formation of TiCo intermetallic compounds, the present invention uses Co and Si as addition. Co itself, that is to say, without any other additive, effects the refining of the $\gamma_2$phase (primarily precipitated), but the effect is enhanced by the simultaneous addition of Co and Si.

For reasons set forth above the present alloy is particularly well suited for use as material for dies and rolls in deep drawing, bending and rolling of such materials as stainless steel, mild steel, nickel alloys, zinc alloys, aluminum alloys, plastics and others.

COMPOSITION OF THE ALLOYS ACCORDING TO THE INVENTION

The present alloy is copper base alloy containing as other principal components aluminum, beryllium, silicon and cobalt. Permissible limits of the amounts of these components are given below in Table 1. In some cases, some other elements may be present as secondary components, as further explained below.

It is a feature common to each element that it accelerates the precipitation of γ_2 in a Cu-Al alloy. When the effect of aluminum for promoting γ_2-precipitation in a Cu-Al alloy is assumed to be unity, the effect of beryllium is 1.8 times that of aluminum, that of silicon 1.5 times, and the effect of cobalt 1.5 times. For example, the figures 1, 1.8, 1.5 and 1.5 are called "aluminum equivalent". Consequently γ_2-precipitation can be expressed as the sum of aluminum equivalents of the components or, in other words, as the formula for aluminum conversion. The conversion formula is

Al % + 1.8% Be + 1.5% Si + 1.5% Co (all in weight %),

and it should be understood as an experimentally determined formula which aims to calculate the γ_2-precipitation of the alloy.

As a method to improve the wear resistance of the present alloys, it is necessary to adjust the precipitation quantity of γ_2. If the value calculated by the above conversion formula is below **9**, the precipitation of γ_2 is not noticeable. If, on the other hand, the value is above **18** the shape of the γ_2-precipitation becomes coarse and the wear resistance as well as the tensile strength of the alloys are greatly decreased. Therefore, the value of the conversion formula is to be regulated in the range of 9 to 18.

The following Table 1 indicates permissible limits of components of the present copper alloy (in percentages by weight).

TABLE 1

Al	Be	Si	Co	Cu
6 to 15	0.6 to 2	9 to 3.5	0.5 to 2.5	balance

Characteristics of the present copper alloy are higher hardness and wear resistance; in many cases, the tensile strength and elongation are likewise improved.

The adjustment of the components permits a variation of the hardness in a range from the hardness of the conventional nickel-aluminum bronze to about 400 H_B.

Preferred Embodiments of the Invention

Some examples of the present copper alloys are shown in Table 2 (in percentages by weight).

TABLE 2

Ex.	Al	Be	Si	Co	Cu	Hardness H_B load 3000 kg
1	7.2	1.6	1.3	0.7	89.2	315 BHN
2	8	0.8	2.2	0.8	88.2	335 BHN

As mentioned above, beryllium, silicon and cobalt are characteristic components of the present copper alloy. These elements decrease the α-phase region in the copper-aluminum system and accelerate the rate of precipitation of the γ_2-phase.

Beryllium changes the lamellar eutectoid structure to the acicular structure and renders the structure finer. Silicon and cobalt render the matrix structure finer and also cause precipitates to form in spherical shape and in finer grain size. These elements are capable of greatly improving the wear resistance of the alloys according to the invention.

The permissible limits of the components are as shown in Table 1. With an aluminum content of less than 6 percent, no precipitates are observed; if, on the other hand, the Al content exceeds 15 percent, precipitates are greatly increased in number and become coarser, thereby causing marked decrease in the strength.

When the beryllium content is less than 0.6 percent, the acicular structure, which is characteristic of the present copper alloys, does not appear; moreover, the wear resistance of the alloys cannot be improved. However, when the Be content is higher than 2 percent, the acicular structure disappears and a considerable decrease in strength occurs, as in the case of an aluminum content of more than 15 percent.

When the silicon content is less than 0.9 percent, the precipitate is neither formed in spherical shape nor is it of fine grain size, but when the Si content is higher than 3.5 percent, the K-phase in the copper-silicon appears, which is undesirable.

When the cobalt content is less than 0.5 percent, the precipitate is not in fine grain size and the tensile strength is not improved. But when the Co content is higher than 2.5 percent, the aluminum equivalent of cobalt changes into a negative number, and the precipitation of the γ_2-phase is retarded.

Mechanical properties of further examples of the present copper alloy are shown in Table 3. These superior mechanical properties are gained not in the heat-treated state but in the as-cast state.

TABLE 3

Example	Al	Be	Si	Co	Cu	Tensile strength kg/mm²	Elongation %	Hardness H_B load 3000 kg
6	8.2	0.79	2.3	2	86.71	65.2	0.3	360 BHN
7	7.3	0.6	1.5	1	89.6	53	4.1	300 BHN

As shown in Table 3, the present copper alloy is very hard. It will be further seen that the alloy in spite of being very hard, is also very ductile.

A particular feature of the alloy is its superior wear resistance over the conventional aluminum-iron-copper alloys, which is due to the addition of beryllium, silicon and cobalt. The greatly improved wear resistance is, moreover, due to the very fine acicular structure of the matrix and the fine spherical precipitates.

Table 4 below shows the composition of a conventional aluminum-bronze alloy used in the comparison tests for wear resistance (in percentages by weight).

TABLE 4

Al	Fe	Others	Cu	Hardness H_B load 3000 kg
13.95	4.6	<0.5	balance	325 BHN

In the accompanying drawings, the superior wear resistance of the alloy according to the invention as well as the role played by different amonts of Co are more fully illustrated. In the drawings,

FIG. 1 is a graphic representation of test results showing the wear resistance of the inventive alloy as compared to conventional wear-resistant aluminum bronz;

FIG. 2 shows the effect of different amounts of Co added;

FIG. 3 shows in front view a rapid wear-testing machine for carrying out the comparison tests; and

FIG. 4 is a side view of the machine of FIG. 3.

FIG. 1, three specimens were subjected to testing. They are designated as Example A, Example B and conventional wear-resistant aluminum bronze.

The composition of the specimens was as follows (in weight percent):

Example	Cu	Al	Be	Si	Co	Sn	Zr	Zn
A	87.91	8.2	0.79	2.3	0.8	—	—	—
B	84.59	8.7	0.61	2.2	0.9	1.7	0.3	1

The composition of the conventional aluminum bronze is indicated in Table 4.

As illustrated in FIG. 1, the load moved over the specimen is entered on the abscissa in kilograms, the wear width of the contact surfaces between specimen and load is entered on the ordinate in millimeters. In the plotted curves, the wear resistance of the alloys given in Examples B (lowermost curve) and A (the curve immediately above) is indicated; in the uppermost curve, that of the conventional alloy is shown, expressed in terms of the wear width, when a load was moved over the specimen at a sliding speed of 0.94 m/second.

In FIG. 2, an alloy of the following composition was subjected to testing:

8.2 Al, 0.79 Be, 2.3 Si, 0.5 to 2.5 Co, balance copper.

In that figure, the effect of Co-addition on the tensile strength is illustrated. The content in cobalt is entered on the absicca in weight percentage, the tensile strength on the ordinate in kg/mm^2. The Al-equivalent is indicate on the right-hand side of the diagram. As mentioned before, the Co-contents of 0.5 to 2.5 weight percent are the satisfactory ones. Above 2.5 percent, the Al-equivalent of Co changes to a negative value and the precipitation of the γ_2-phase is retarded.

In FIGS. 3 and 4, the test machine (Ogoshi-type Rapid Tester) is shown to consist of a cylindrical disk A of stainless steel, on which a load P is applied in the direction of the arrow X. The specimen to be tested is designated by B, the wear width by the letter *f*. In the test, a sliding speed of 0.94 m/sec was applied, the load was 2.8 to 25.5 kg.

From the curves showing the result of the wear-resistance test, it will be readily seen that the wear resistance of the present copper alloy is decidedly far superior to the conventional aluminum-iron-copper alloy.

While the present alloy, as described above, is an alloy containing Cu, Al, Be, Si and Co as the principal components, we may add thereto as secondary elements Sn (< 5), Zn (< 5), Mn (< 5), Fe (< 3) and Zr (< 0.3). One or more of these additional elements may be incorporated in the alloy. Test results have revealed that these additional elements have the following effects on the copper alloy according to the invention.

EFFECT OF TIN ADDITION

Tin is effective to improve the wear resistance and replace a part of the silicon if the intended objects require this.

However if the Sn content is increased over the limit value, the wear resistance will be impaired. An example of proper Sn addition is shown in Table 5.

The value of wear width in Table 5 is a value *f*, expressed in millimeters, and shown in FIG. 3. It will be understood that the smaller value the wear width has the higher is the wear resistance.

TABLE 5

Al	Be	Si	Co	Sn	Cu	Hardness H_B	Wear width
8.2	0.79	2.3	0.8	—	87.91	340 BHN	2.88
8.2	0.78	2.2	0.8	2	86.02	360 BHN	2.35

Effect of Zinc Addition

Zinc improves the tensile strength and elongation but if the amount added exceeds the limit value, the elongation will be greatly decreased. An example is shown in Table 6.

TABLE 6

Al	Be	Si	Co	Zn	Cu	Tensile strength kg/mm²	Elongation %
8.2	0.79	2.3	0.6	—	88.11	56.4	0.7
8.1	0.81	2.25	0.6	2.5	85.74	59.1	3

Effect of Manganese Addition

Manganese improves the tensile strength but if the added amount exceeds the limit value, the tensile strength will be decreased. An example is shown in Table 7.

TABLE 7

Al	Be	Si	Co	Mn	Cu	Tensile strength kg/mm²
8.2	0.79	2.3	0.7	—	88.01	36.4
8.2	0.81	2.2	0.7	2.5	85.59	59.8

Effect of Iron Addition

Iron makes the grain size finer but if the added amount exceeds the limit value, the wear resistance will be degraded. The limit value is up to 3 weight percent.

Effect of Zirconium Addition

Zirconium makes the grain size finer, and even if it is added in an amount exceeding its limit, the effect will remain unchanged.

The effect of two or more additional elements is shown in Table 8 below.

TABLE 8

Al	Be	Si	Co	Sn	Zn	Mn	Zr	Fe	Cu	Hardness BHN	Tensile strength kg/mm²	Elongation %
7.8	0.8	2	0.8	1.5	3.2	2	—	—	81.9	330	54.2	1
10.8	0.4	1.5	2	1.8	—	—	0.3	—	83.2	350	57.8	0.5
7.5	1.5	1.1	0.5	4.2	2	3	—	2.5	77.7	320	53.5	4

Wherever in the specification and claims the expression "balance Cu" is used it means that the Cu content, while being within the limit range defined in the main claim, is dependent on the amount of secondary element or elements added to the principal components. In other words, the copper value in some examples, as well as in the appended claims, is given by omitting the respective amounts and values of the impurities present, if any, such as for example 0.5 weight percent or less of Pb, P, As and possibly others.

What we claim is:

1. A copper base alloy consisting of 8.2 weight % Al, 0.79 wt% Be, 2.3 wt% Si, 2 wt% Co, and 86.71 wt% Cu, the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

2. A copper base alloy consisting of 7.3 weight % Al, 0.6 wt% Be, 1.5 wt% Si, 1 wt% Co, and 89.6 wt% Cu, the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

3. A copper base alloy consisting of 8.2 weight % Al, 0.78 wt% Be, 2.2 wt% Si, 0.8 wt% Co, 2 wt% Sn, additionally containing as secondary elements at least one of the elements: up to 5 wt% Zn, up to 5 wt% Mn, up to 3 wt% Fe, and up to 0.3 wt% Zr, and the balance Cu the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

4. A copper base alloy consisting of 8.1 weight % Al, 0.81 wt% Be, 2.25 wt% Si, 0.6 wt% Co, 2.5 wt% Zn, additionally containing as secondary elements at least one of the elements: up to 5 wt% Sn, up to 5 wt% Mn, up to 3 wt% Fe, and up to 0.3 wt% Zr, and the balance Cu the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

5. A copper base alloy consisting of 8.2 wt% Al, 0.81 wt% Be, 2.2 wt% Si, 0.7 wt% Co, 2.5 wt% Mn, additionally containing as secondary elements at least one of the elements: up to 5 wt% Sn, up to 5 wt% Zn, up to 3 wt% Fe, and up to 0.3 wt% Zr, and the balance Cu the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

6. A copper base alloy consisting of 7.8 weight % Al, 0.8 wt% Be, 2 wt% Si, 0.8 wt% Co, 1.5 wt% Sn, 3.2 wt% Zn, 2 wt% Mn, additionally containing as secondary elements at least one of the elements: up to 3 wt% Fe, and up to 0.3 wt% Zr, and the balance Cu the alloy being characterized by readiness to be used in the as-cast state without being subjected to heat treatment, and having excellent wear resistance under load, and high toughness.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,830,644 Dated August 20, 1974

Inventor(s) S. Watanabe et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 56: numerical data in Table 1: for "Si", the correct values are -- 0.9 to 3.5 -- (instead of "9 ..."); and

column 8, lines 23, 33, 52 and 62 (that is claims 3, 4, 5 and 6, lines 5, for all claims), before "the alloy being char--acterized" (or, after "balance Cu"), insert commas (,).

Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
★ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334