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COPPER BASE ALLOYS

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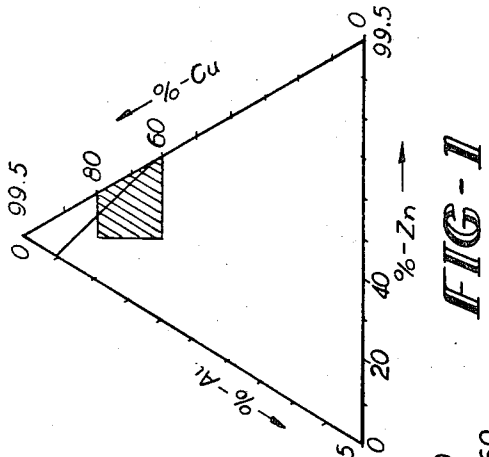


FIG - 1

FIG - 2

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COPPER BASE ALLOYS

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The present application relates to new and improved copper base alloys. More particularly, the present invention resides in greatly improved copper base alloys containing zinc, aluminum and cobalt, said alloys having greatly improved physical properties and being suitable for a wide range of applications, including castings, forgings, extrusions, and hot or cold rolled or drawn products. The improved alloys of the present invention are particularly suitable for use in wrought products.

Over the years, numerous attempts have been made to improve the strength characteristics of ductile brass without sacrifice of formability. These attempts have concentrated on utilizing a great variety of alloying additions in order to achieve this goal. Some of these alloying additions are quite expensive and add considerably to the cost of the alloy.

In addition, the art has thoroughly explored many unusual thermo-mechanical processes in order to improve the strength characteristics without sacrificing formability.

The high strength brasses which have been developed in the art generally are multiphase alloys having limited ductility and cold formability. Such alloys are most suitable for application as castings or hot worked products.

Despite these extensive investigations, 70/30 brass has prevailed over the years as the best and most economical copper base alloy for severe forming applications.

Accordingly, it is a principal object of the present invention to provide an improved copper base alloy.

It is an additional object of the present invention to provide a copper base alloy having improved strength levels in either the fully annealed or cold worked tempers.

It is an additional object of the present invention to provide improved copper base alloys as aforesaid which achieve improved strength characteristics with minimal sacrifice in formability.

It is an additional object of the present invention to provide an improved copper base alloy as aforesaid, said alloy being characterized by relatively low cost so that it is economically suitable on a large scale.

Further objects and advantages of the present invention will appear hereinafter.

In accordance with the present invention, it has now been found that the foregoing objects may be readily and conveniently achieved. The improved alloy of the present invention consists essentially of the following ingredients in the following ranges, wherein all percentages are weight percentages: copper from 67 to 80%, zinc from 15.0 to 31%, aluminum from 1.0 to 5.0%, and cobalt from 0.1 to 3%.

It has been found that the foregoing alloy achieves greatly improved physical properties with minimal sacrifice in formability. For example, the improved alloy of the present invention has yield strength characteristics in the fully annealed condition on the order of 45,000 p.s.i. and over; whereas conventional copper base alloys for forming applications normally achieve yield strengths in the fully annealed condition in the range of 10,000 to 25,000 p.s.i. and rarely over 30,000 p.s.i. The alloys of the present invention have correspondingly high yield strengths in the cold worked temper, for example, 90,000 p.s.i. and over after 50% cold reduction; whereas conventional alloys normally fall in the range of 50,000 to 75,000 p.s.i.

In addition, and importantly the alloys of the present invention are characterized by a high formability. Using the highly formable 70/30 brass as a standard, the alloys of the present invention have comparable formability. This is particularly surprising in view of the high strength of the alloys of the present invention.

These surprising characteristics in an inexpensive alloy are particularly unexpected in view of the extensive art in this field attempting to approximate these characteristics.

The alloys of the present invention are known as modified aluminum-brasses and basically have either of the following structures: (1) an alpha (face-centered cubic) structure; or (2) an alpha plus a limited amount of beta (body-centered cubic) structure.

The addition of aluminum to copper-zinc alloys has long been known for its strengthening effect on such alloys. The disadvantage of the aluminum addition is that in saturated alpha phase alloys, which have highest strengths, small variation in aluminum content generally results in large variations in ductility and strength. These large variations are a result of the structure of the saturated alloy changing markedly with aluminum content. For example a change in aluminum content of one percent may cause an increase in beta phase content of up to 33 percent.

In accordance with the present invention it has been surprisingly found that the addition of cobalt in the range of 0.1 to 3% by weight overcomes the disadvantages of the ternary copper-aluminum-zinc alloys such that properties and structure are more uniform over a practical range of aluminum content. In addition, a very marked grain refining effect occurs upon the addition of cobalt which is highly advantageous.

In accordance with the present invention the alloying ingredients must critically fall within the foregoing ranges. The copper content must fall within the range of 67 to 80% by weight and preferabmly from 70 to 76% by weight. Below 67% by weight the strength falls off markedly and above 76% by weight in saturated alloys an additional phase, termed gamma having a complex cubic crystal structure, may be encountered with slow cooling cycles which limits the ductility of the alloy.

Similarly, the zinc content is within the range of 15.0 to 31% by weight and preferably from 19 to 28%. The aluminum content should be maintained in the range from 1.0 to 5.0% by weight and preferably 2.0 to 4.5% and the cobalt content should be maintained in the range 0.1 to 3% and preferably 0.1 to 1.0%.

For maximum ductility-formability at any given copper-aluminum level, the cobalt content should be between

0.1 and 1.0% while for greater strength and lesser ductility the cobalt may approach higher levels up to 3%. Above this level of cobalt, little improvement in properties is realized since excess cobalt appears as elemental metal particles or as massive cobalt plus aluminum intermetallic compound and in addition, ductility decreases.

In general, the lower cobalt content alloys are high strength, high ductility materials; whereas the higher cobalt content alloys provide even higher strengths, but lower ductility.

The composition of specific alloys within the above ranges are subject to the further internal restriction that at about the 69% level of copper the aluminum content should preferably be in the range of 1.2 to 3.2% in order to insure high ductility-strength characteristics and at about the 74% level of copper the aluminum content should preferably be between 3.0 and 5.0% for the same reasons. Proportionate adjustments of aluminum content for the various copper contents between the specified limits should preferably be made.

Furthermore, in order to attain the preferred properties the aluminum content should preferably be related to the zinc content in accordance with the following equation:

$$\text{Weight percent Al} = -0.29 \text{ wt. percent Zn} + 9.2 \pm 1.35$$

The subject alloys are represented in the attached drawings which are isothermal (932° F.), constant cobalt (0.5%) sections of the quaternary phase diagram. FIGURE 1 shows the relative location of the alloys of the present invention on the ternary phase diagram. FIGURE 2 shows the shaded section of FIGURE 1. In FIGURES 1 and 2 the solid line represents the alpha phase boundary. In FIGURE 2, the dotted line represents the alloys of the present invention at constant 0.5% cobalt. Similar diagrams may be readily constructed for other cobalt levels.

The structure of the alloys of the present invention in the cold worked and annealed condition is either (1) a matrix of fine grained, face-centered cubic, alpha phase (saturated or very nearly so), or (2) saturated alpha plus beta phase, with both structure (1) and structure (2) having very fine intermetallic compound and/or precipitate particles dispersed throughout.

The alloys of the present invention may include in addition to the foregoing materials conventional impurities typically found in commercial copper base alloys. In addition, various other alloying ingredients may be added to achieve particularly desirable results. Common impurities may include: lead; tin; phosphorus; iron; manganese; nickel; and silicon. For minimizing dezincification in corrosive environments, the addition of arsenic, antimony and/or phosphorus may be desirable in an amount from 0.02 to 0.10%.

In general, the alloys of the present invention have an alpha plus particulate phase or an alpha plus beta plus particulate phase structure and are utilizable in a wide variety of applications. In view of their high strength and high formability, they are preferably provided in the wrought form. The oxidation resistance and castability of the alloys of the present invention are excellent suggesting widespread application as high strength, low cost foundry alloys while their excellent hot forming properties also make them desirable for forgings as well as extrusions. In general, better combinations of mechanical properties at low costs are obtainable with the alloys of the present invention than are available in any currently produced copper base alloys regardless of price.

Processing of the subject alloys requires no unusual treatment. As an example, the processing to sheet is as follows. Melting and casting are performed under similar conditions as brass alloys. Direct chill (DC) casting is particularly suitable. Hot rolling is easily accomplished using normal brass mill procedures. Under rapid cooling conditions a non-equilibrium structure may be obtained which reduces initial cold rollability. This may be overcome by an anneal in the range of 1000 to 1200° F. wherein practical equilibrium proportions of alpha and beta phases are attained.

It has been observed in the processing of the subject alloys that they exhibit an unusually high response to low temperature stress relief annealing following cold working. Normally, copper base alloys which have been heavily cold worked may respond with an increase in yield strength of up to 15% when annealed at temperatures below the recrystallization temperature. This increase also normally is of practical consequence only within a relatively narrow range of annealing temperatures (50 to 100° F.). In the alloys of this invention, increases in yield strength of 30 to 40% have been noted upon low temperature annealing of material cold rolled 50%. Further, this response occurs over a wider range of temperature (150 to 200° F. span), thereby increasing its commercial applicability. The magnitude of improvement in strength properties will be illustrated in the examples which form a part of the present specification.

Because of the stabilizing influence of cobalt on the structure, the properties of recrystallization annealed material are also stable over quite an extended temperature range. For example, the yield strength of a typical composition only decreased from 64,000 p.s.i. to 60,000 p.s.i. after one hour anneals at 700° F. and 1000° F. respectively. Tensile strength is similarly uniform while elongation steadily increases over the same range of temperature.

A further outstanding characteristic of the subject alloys is a very marked improvement in stress corrosion resistance. The copper-zinc brasses are highly susceptible to stress corrosion cracking when exposed to certain corrosive environments. This susceptibility is proportional to zinc content and hence alloys containing more than 15% zinc are rarely chosen for stressed applications in corrosive environments. It has been found that the cobalt modified aluminum brasses have greatly improved resistance to stress corrosion cracking when compared to the binary copper-zinc alloys. This behavior will be apparent from the ensuing examples. Coupled with this stress corrosion resistance is a high level of resistance to general corrosion.

The present invention will be more readily understandable from a consideration of the following illustrative examples.

Example I

Alloys having the compositions listed below were prepared from cathode copper, slab zinc, either cobalt metal, copper-cobalt master alloys, or aluminum-cobalt master alloy, and aluminum metal pellets. Preparation followed the ensuing sequence. Cathode copper chunks were melted under charcoal, a portion or all of the desired aluminum content was added and stirred in, cobalt in the form of metal pellets, copper-15% cobalt master alloy or aluminum-30% cobalt master was added next and the melt was held at temperature until complete solution occurred, zinc chunks were added and stirred in. The melt at a temperature of about 2000° F. was poured into a cast iron mold and allowed to solidify.

The resulting ingots were reheated to 1500° to 1650° F. and hot rolled from 1.750" to 0.300", finishing at about 1000° F. Material was then cold rolled to 0.120", annealed at 1000° F. for one hour, cold rolled to 0.060", annealed at 1000° F. for one hour and cold rolled to 0.030". Material was evaluated in the final 50% cold rolled condition at 0.030" and also in the annealed condition where various temperatures were used.

For comparative purposes, commercial 70/30 brass and a copper-aluminum-zinc alloy were subjected to the same treatment, except that the 70/30 brass was interannealed at 800° F. instead of 1000° F.

The properties are given in the following table, i.e., yield strength at 0.1% offset, tensile strength and percent elongation both in the cold rolled an annealed tempers.

TABLE I

Alloy	Composition wt. percent	50% Cold Rolled			1,000° F. Anneal, 1 hr.			1,200° F. Anneal, 1 hr.		
		Yield Strength, p.s.i.	Tensile Strength, p.s.i.	Percent Elongation	Yield Strength, p.s.i.	Tensile Strength, p.s.i.	Percent Elongation	Yield Strength, p.s.i.	Tensile Strength, p.s.i.	Percent Elotgation
I	73.25 Cu, 3.75 Al, 0.44 Co, 22.6 Zn	90,500	129,000	2.5	60,000	87,000	33	51,500	83,000	35
II	76.9 Cu, 4.6 Al, 0.4 Co, 18.1 Zn	99,500	133,500	2.2	[1] 56,000	33,500	25.2			
III	69.5 Cu, 1.7 Al, 0.4 Co, 28.4 Zn	87,000	115,500	2.2	[1] 43,500	72,000	34.5			
IV	73.3 Cu, 3.5 Al, 0.4 Co, 22.8 Zn	90,000	126,000	2.3	[1] 49,500	39,500	29.5	49,000	79,500	38
					58,000	84,000	34.5			
V	74.0 Cu, 4.0 Al, 1.0 Co, 21.0 Zn	93,000	130,000	2.1	[1] 62,500	89,500	26	57,000	86,000	32
VI	75 Cu, 4.3 Al, 0.2 Co, 20.5 Zn	93,000	127,500	2.0	[1] 44,500	76,000	37.5			
					52,900	83,100	37.6	42,600	80,600	37.4
VII	76 Cu, 4.0 Al, 20 Zn	89,000	114,000	2.0	[2] 27,000	65,000	57			
					[2] 41,000	32,000	29			
VIII	70 Cu, 30 Zn	74,500	90,000	3.5	[2] 21,800	53,000	50			

[1] 1,100° F. Anneal, 17 hour cycle, 3 hour hold. [2] 800° F. 1 hr.

Example II

To illustrate the unusually high response to low temperature annealing Alloy IV from Example I was subjected to a one hour anneal at 400° F. with the following results.

TABLE II

	Tensile Properties					
	50% Cold Rolled, 0.1% offset			50% Cold Rolled + Annealed 1 hr. at 400° F.		
	Yield Strength, p.s.i.	Tensile Strength, p.s.i.	Percent Elongation	Yield Strength, p.s.i.	Tensile Strength, p.s.i.	Percent Elongation
Alloy IV	90,000	126,000	2.3	134,000	147,300	1.4

Example III

Several of the alloys prepared in Example I were evaluated for formability using two common measurements, i.e., limiting draw ratio determination for evaluating deep drawability, and Olsen cup testing to check stretch formability. These results show the improved alloys of the present invention to be fully equivalent in drawability to 70/30 brass (listed for comparison and only slightly less formable in stretch forming than 70/30 brass.

TABLE III

Alloy	Limiting Draw Ratio	Olsen Bulge Height
III	2.276	0.374"
IV	2.270	0.400"
VIII	2.260	0.420"

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A copper base alloy consisting essentially of copper from 67 to 80% by weight, zinc from 15.0 to 31% by weight, aluminum from 1.0 to 5.0% by weight, cobalt from 0.1 to 3.0% by weight.

2. An alloy according to claim 1 wherein the aluminum and zinc contents are in accordance with the equation: wt. percent Al=−0.29 wt. percent Zn+0.2±1.35.

3. An alloy according to claim 2 wherein said zinc is present in an amount from 19 to 28%.

4. An alloy according to claim 2 wherein said aluminum is present in an amount from 2.0 to 4.5% by weight.

5. An alloy according to claim 2 wherein said cobalt is present in an amount from 0.1 to 1.0%.

6. An alloy according to claim 2 wherein said copper is present in an amount from 70 to 76%.

7. An alloy according to claim 2 including a material selected from the group consisting of arsenic, antimony and phosphorus in an amount from 0.02 to 0.10% by weight.

8. An improved copper base alloy consisting essentially of copper from 70 to 76%, aluminum 2.0 to 4.5%, zinc 19 to 28% and cobalt 0.1 to 1.0%, wherein the aluminum and zinc contents are in accordance with the equation: wt. percent Al=−0.29 wt. percent Zn+9.2 ± 1.35

References Cited

FOREIGN PATENTS

12,160 7/1963 Japan.
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CHARLES N. LOVELL, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,402,043 September 17, 1968

Richard Dale Smith

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

Column 2, line 50, "preferabmly" should read -- preferably --. Column 5, line 39, after "comparison" insert a closing parenthesis. Columns 5 and 6, TABLE I, the seventh and eighth columns should appear as shown below:

87,000	33
83,500	35.2
72,000	34.5
79,500	39.5
84,000	34.5
89,500	26
76,000	37.5
83,100	37.6
65,000	57
72,000	39
53,000	50

same table, heading to the last column thereof, "Percent Elotgation" should read -- Percent Elongation --. Column 6, line 31, wt. percent Al=-0.29 wt. percent Zn+0.2±1.35" should read -- wt. percent Al=-0.29 wt. percent Zn+9.2±1.35 --.

Signed and sealed this 17th day of February 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents