Sept. 8, 1942. E. G. MITCHELL 2,295,180

COPPER ALLOY

Filed May 20, 1940

FIG. 1

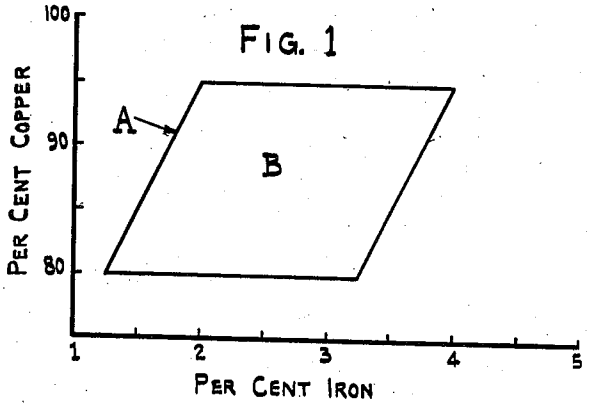


FIG. 2

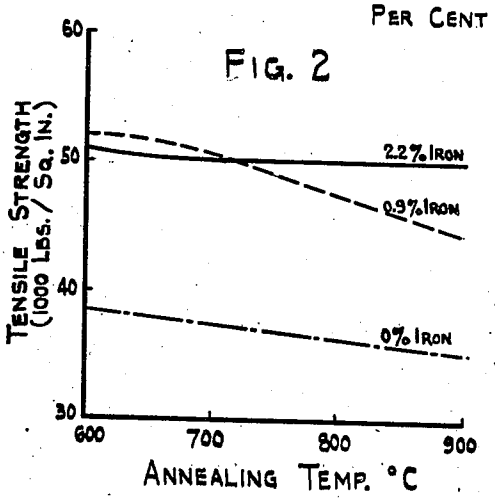


FIG. 3

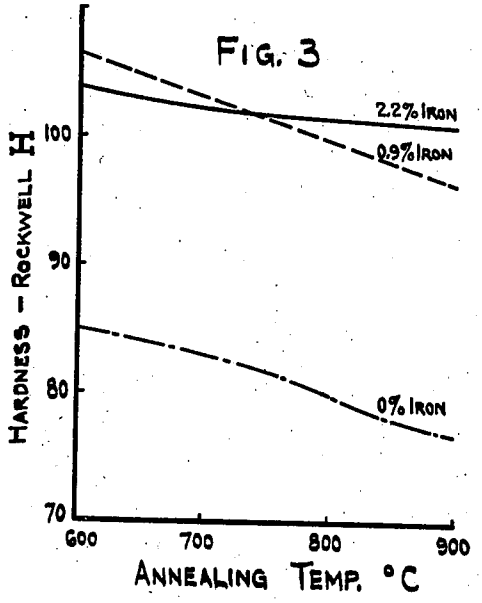
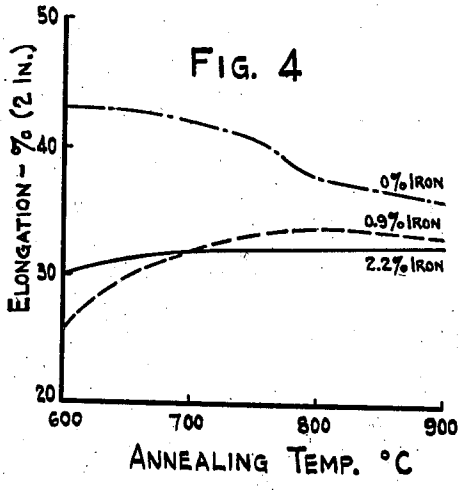


FIG. 4



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Patented Sept. 8, 1942

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UNITED STATES PATENT OFFICE

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COPPER ALLOY

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Application May 20, 1940, Serial No. 336,151

7 Claims. (Cl. 75—155)

This invention relates to alloys of copper, and particularly to copper-zinc-iron alloys containing high percentages of copper. More specifically, this invention relates to novel compositions consisting of copper-rich alpha copper-zinc alloys containing sufficient iron to impart desirable properties hitherto unobtained with copper-base alloys.

An object of this invention is to provide alloys of high copper content which are characterized by improved physical properties and which tend to retain such properties substantially unimpaired when subjected to elevated temperatures.

Another object of the invention is to provide alpha copper-zinc alloys containing sufficient iron to impart desirably improved physical properties as well as resistance to change in such properties on heating.

Another object of this invention is to provide alpha copper-zinc alloy compositions containing iron which are characterized by favorable ductility, elongation, and strength properties and which may be heated and reheated to elevated temperatures without deleterious effect on these properties at ordinary or elevated temperatures.

A further object is to provide copper-rich alloys containing zinc and iron which are characterized by grain structure of improved stability at elevated temperatures.

A further object of this invention is to provide copper rich alloys containing zinc and iron which are particularly adapted for the manufacture of brazed articles.

Another object is to provide copper-rich alloys containing zinc and iron which are suited for the manufacture of ductile sheets suitable for assembly by brazing or welding operations.

Other objects will appear from the following detailed description.

In the drawing:

Fig. 1 is a graph showing the composition of alloys in accordance with this invention; and Figs. 2, 3, and 4 are graphs showing the tensile strength, hardness, and elongation, respectively, of alloys after treatment at various temperatures, illustrating improvements obtainable in accordance with this invention.

Although certain copper-zinc-iron alloys have long been known, these have consisted of compositions having low copper contents of about 60% copper, that is, in the alpha-beta range of alloys, such as were described in British Patent 278 (1860). In alloys containing a higher percentage of copper, for example, 70% copper, iron has generally been considered an undesirable impurity; where the obtainment of beneficial effects, such as hardening or grain refinement, were intended to be secured in such alpha alloys by the addition of iron, it has been the general opinion, as expressed for example in Foundry (London), vol. 51, page 898 (1923), that an iron content of 1% should not be exceeded. Furthermore, as can be seen from the most recent publication on the equilibrium relationships in the ternary system copper-zinc-iron, that by Bauer and Hansen, Z. fur Metallkunde, vol. 26, pages 121–129 (1934), knowledge has been lacking concerning ternary alloys containing a high percentage of copper and more than 1% of iron.

In an extended investigation of the copper-zinc-iron alloys, containing more than 80% copper, I have found that compositions having unique and desirable properties may be obtained when more than certain minimum quantities of iron are used. Compositions containing smaller proportions of iron display erratic behavior and yield unfavorable results, a fact which has been brought out during my investigation and which may well be responsible for the disrepute which has been accorded the use of substantial amounts of iron in copper-zinc alloys of high copper content.

The principal disadvantage which I have found in alloys containing smaller amounts of iron than compositions in accordance with my invention is their tendency on heating, to lose the original favorable physical properties. Thus, although sheets of such alloys may be prepared having excellent ductility and tensile strength characteristics, they become weakened and embrittled on heating to elevated temperatures. Microscopic examination of these alloys prior to such treatment reveals the presence of a large number of exceedingly fine particles disseminated throughout the individual metal grains, which particles are probably responsible for the increased strength. However, on heating such alloys to elevated temperatures, sufficient segregation and migration of these particles to the

grain boundaries occurs as to result in the embrittlement and loss of strength of the metal.

Extended research has shown that such difficulties may be overcome by a sufficient increase in the iron content, since such increase has the surprising effect of markedly reducing the tendency for segregation and migration of the precipitated constituents to the grain boundaries. Thus, alloys containing a minimum of iron increasing linearly from 1.25% iron at 80% copper to about 2% iron at 95% copper, or an amount of iron up to about 2% more than the specified minimum, display, in addition to favorable physical properties, a desirable resistance to impairment of such properties on heating. These are compositions to the right of line A in Fig. 1. Microscopic examination of these alloys has revealed, in addition to a primary constituent, i. e. fine particles similar to those above referred to, the presence of a secondary constituent, consisting of relatively large crystalline particles, which in the case of sheets appear in the form of threads elongated in the direction of rolling. These two types of particles and likewise their distribution throughout the metal remain essentially unaltered even after the metal has been subjected to treatment at elevated temperatures. In other words, in the presence of a sufficient amount of iron, as specified above, to produce the two types of constituents distributed throughout the metal, the tendency of the primary fine particles to segregate in the grain boundaries, which is characteristic of the low-iron alloys which are free of the secondary constituent, no longer predominates and detriment to the physical properties on heating need not be feared. In the alloys in accordance with this invention, the primary particles appear at high magnification as gray spheres, which turn black on treatment with ammonia-hydrogen peroxide etching liquid, while the secondary particles are of a gray blue color, both in the etched and unetched condition.

While the composition of these constituents has not been determined, it appears probable that they consist of iron-zinc-copper solid solutions or inter-metallic compounds consisting largely of iron and zinc. These constituents, furthermore, appear to be of substantially higher melting point than the fine particles present in the alloys containing less iron than specified in accordance with this invention, which may account, at least in part, for the improvement in the heat-stability of grain structure of the alloys of this invention. Apparently, an increase in the proportion of iron to zinc in these alloys is accompanied by an increase in the proportion of iron to zinc in the constituents and a rise in their melting points.

It is to be noted that on heating the low-iron alloys, in which the fine particles have become segregated, above recrystallization temperatures, the iron is no longer effective in refining the grain growth and large individual crystals result. On the contrary, in the alloys in accordance with this invention, both primary and secondary precipitates remain distributed throughout the matrix and retain the effect of producing a refined grain structure on heating above recrystallization temperatures.

Accordingly, the advantageous features of the present invention are obtainable in copper-zinc-iron alloys containing 80% to about 95% copper, an amount of iron within a range which varies according to the copper content from 1.25% to 3.25% at 80% copper to 2% to 4% at 95% copper, and substantially the balanced zinc. Referring to Fig. 1, these alloys are to the right of line A and included in area B. Generally, the most desirable alloys are those containing 2% to 2.5% iron, and within this range of iron content, the most important compositions have been those containing 90% to 92% copper.

The following Table 1 lists physical properties of alloys of the present invention obtained with test sheets, about 0.025 inch in thickness, prepared by successive rolling and annealing treatments, the final annealing being such as to produce a commercial soft temper. These alloys contained the stated percentages of copper and iron and substantially the balance zinc, and the temper of the sheets was suitable for deep drawing. Since the tensile strength is much higher than that of deep-drawing iron-free copper-zinc alloys, much stronger articles may be manufactured from alloys of this invention.

Table 1

PHYSICAL PROPERTIES OF COPPER-ZINC-IRON ALLOYS OF THIS INVENTION

Percent iron	Percent copper	Tensile strength (1,000 lbs./sq. in.)	Elongation (percent in 2 in.)	Rockwell hardness (1/16-60-B)
1.5	80	57.6	34	106.5
2.6	84.2	54.5	31	105.5
1.75	90	47.5	32	100
2.0	90	48.0	32	101
2.25	90	48.5	32	102
2.5	90	49.0	31	103
2.9	94.5	48.0	29	101
AVERAGE PROPERTIES				
2-2.5	80	58.0	34	107
2-2.5	85	54.0	32	104
2-2.5	90	48.5	31.5	102
2-2.5	95	45.2	31	97

Physical properties of test sheets which were annealed at temperatures above and below the recrystallization point are included in the following Table 2, which gives a clear indication of the superiority of the alloys in accordance with this invention over compositions containing insufficient iron to produce the desired effect. The alloys contained the stated percentages of iron and copper and balance zinc.

Table 2

Per cent iron	Per cent copper	Tensile strength		Elongation		Rockwell hardness	
		600°	800°	600°	800°	600°	800°
[1] 1.4	80.7	60.8	57.2	33	35	109	105
0.9	81.8	54.8	49.4	22	39	107	102
[1] 2.6	84.2	55.0	54.0	30	31	108	105
1.25	85	54.0	50.0	32	34.5	106	101
[1] 2.2	90	50.8	50.8	30	32	104	102
0.9	90	52.0	47.4	26	34	106	100
[1] 2.9	94.5	48.8	47.0	28	30	102	100
1.4	95.9	51.6	44.2	25	34	106	96

[1] Alloy in accordance with this invention.

The following Table 3 contains detailed data, shown graphically in Figs. 2, 3, and 4, on the physical properties of alloys, containing 90% copper, the indicated amount of iron, and balance zinc, after treatment at various annealing temperatures, illustrating the unique character of the alloys of this invention as compared with compositions containing insufficient iron and the iron-free alloys. Comparative results similar to those tabulated are likewise obtained with alloys containing from 80% to about 95% copper.

Table 3

	Annealing temperature, °C.						
	600°	650°	700°	750°	850°	850°	
Tensile strength	50.8	50.5	49.7	49.6	50.8	50.5	90% Cu, 2.2% Fe,[1] Bal. Zn
Elongation	30.2	31.0	32.0	32.5	32.2	32.3	
Rockwell hardness	104	103	102.5	102	101.5	101.5	
Tensile strength	52.0	51.8	51.0	48.7	47.4	46.3	90% Cu, 0.9% Fe, Bal. Zn
Elongation	25.7	30.7	32.0	33.5	34.0	33.5	
Rockwell hardness	106.5	104	103.5	101	100	98	
Tensile strength	38.5	38.0	37.5	37.0	36.5	36.0	90% Cu, 10% Zn
Elongation	43	43	42	41	38	37	
Rockwell hardness	85	84	83	82	80	78	

[1] Alloy in accordance with this invention.

It will be seen that although the iron-free alloy and the alloy containing insufficient iron display significant loss of tensile strength and hardness with rising annealing temperature, the alloy of this invention maintains a practically constant high tensile strength and only a slight decrease in hardness over the entire range of annealing temperatures. At the same time, an adequate extent of ductility is retained, as reflected in the elongation measurements.

The distinctive qualities of alloys of this invention with respect to the resistance displayed against impairment of physical properties on heating, are still more forcefully brought out in tests involving heating to an elevated temperature, cooling, reheating, and measuring the properties at elevated temperature. The results of such tests are markedly in favor of the present alloys as compared with compositions containing insufficient iron. For example, elongation tests carried out at 700° C. on 90% copper alloy sheets, which had been heated to 980° C. and then air-cooled, yielded values for the alloy containing 2 to 2.5% iron which were over two and a half times that for the alloy containing 0.9% iron. A cycle of this type, involving two heating periods and an intermediate cooling, is for example, encountered when the manufacture of an article involves a brazing or welding operation, cooling, and then a second brazing or welding operation. Alloys in accordance with this invention satisfactorily meet the requirements of such processes, while alloys containing smaller proportions of iron are unsuitable mainly because of intercrystalline fracture; iron-free alloys are undesirable for such use because of the added thickness, and therefore expense, required to obtain the requisite strength.

Accordingly, this invention is based on the discovery of the unique characteristics imparted to copper-zinc alloys, containing from 80% to about 95% copper by the addition of at least a minimum quantity of iron, which, as specified above, varies linearly from 1.25% at 80% copper content to 2% at 95% copper content. Amounts of iron up to about 2% greater than the minimum may be utilized without difficulty, and it will generally be desirable to have an iron content of between 2 and 2.5%.

These alloys may readily be manufactured by melting the component metals in the required proportions in a suitable furnace and then casting the metal in the desired form. For securing uniform results, it is preferable first to melt completely an amount of copper corresponding to about one-third of the total charge, then to add and disperse therein the required amount of iron, for example in the form of pieces of scrap of suitable purity, and finally add the balance of the copper and the zinc. It is desirable that precautions be taken during the melting process to prevent excessive solution of gas in the melt such as would tend to yield inferior castings; for example, a layer of charcoal may be maintained at the surface of the metal during the melting process. Other methods of adding the iron may be employed, for example galvanized sheet iron or copper-iron alloy may be added to the molten copper and maintained submerged therein until completely dissolved. Also, it may at times be convenient to include a proportion of scrap alloy of known composition in the furnace charge. After raising the temperature to 1290° C. to complete the melting, the molten metal is poured into prepared molds of the desired size and shape. When the product is desired in the form of sheets, the metal may be cast in the form of slabs, from which sheets having the required dimensions and temper may be produced by successive rolling operations with suitable intervening and final annealing treatments.

An alloy which has been found particularly adapted for the manufacture of pressure vessels is of the following composition:

	Per cent
Copper	90–92
Iron	2.0–2.5
Zinc	5.5–8

The total amount of other metals is preferably maintained below 0.10% with the lead content maintained below 0.05%.

Thin sheets of this alloy may be produced by casting a slab and successively rolling to the desired thickness, the metal being annealed between successive reductions by suitable heat treatment. For example, a 1.75 inch slab may thus be rolled to a final thickness of about 0.023 inch, the desired annealing treatments being carried out between successive reductions of 40%–75%. Other desired operations may likewise be inserted in the manufacturing schedule, for example after the initial reduction, the surface scale may be removed by milling, while prior to the final reduction it will generally be desirable to trim the sheet to smooth edges and to remove the scale by passing the sheet through an acid bath. Following the final reduction, the desired temper may be produced by applying a suitable annealing treatment. After being cleaned by passing through an acid bath, the sheet may be cut to the desired dimensions.

Sheets produced in this manner possess a desirable combination of good ductility and excellent strength, are capable of strong bonding by means of a brazed joint, and may be reheated for a second brazing or welding operation without difficulty and without detriment to the fabricated article. Accordingly, the sheets can

readily be drawn, bent, or otherwise shaped, to form complementary parts ready for assembly by brazing or welding into a completed article. The properties of this alloy render it especially suitable for the fabrication of brazed or welded pressure vessels.

In the fabrication of vessels, two or more sheets of this alloy, produced as described above, may be formed in the desired shape, as by a draw-press operation. The complementary parts are then assembled, after the surface has been cleaned, and a suitable brazing alloy is provided at the portions intended to be bonded. The assembly may then be passed through a furnace heated to a temperature suited for the brazing operation, so as to result in a vessel having strongly bonded joints. If desired, the brazing operation may be effected in an inert or reducing atmosphere.

If the attachment of additional parts by brazing or welding is required, this operation may be carried out without difficulty when using this alloy, to produce a completed vessel having the desired strength. On the contrary, unfavorable results were obtained with similar sheets prepared from alloys containing insufficient iron to insure the presence of both the primary and secondary precipitates above referred to, that is, amounts of iron less than the specified minimum quantities. In such sheets intercrystalline cracks tended to form during the second heating cycle, apparently due to the presence at the grain boundaries of a substantial proportion of the low-melting precipitated constituent, as well as to the fact that because of grain growth during the first heating cycle relatively short intercrystalline paths were provided between opposite points on the sheet surfaces. Such grain growth and cracking of the sheet does not occur with the alloy of this invention on being subjected to the reheating operation.

Pressure vessels fabricated in this manner have been found on test to withstand much greater pressures without bulging or bursting than vessels similarly manufactured from sheets of iron-free alloys of copper and zinc.

It may at times be desirable to include small amounts of additional elements for securing modification of the properties of the alloy compositions of this invention, provided however, that such additions do not impair the desirable features described above. For example, additions of phosphorus may be desirable up to amounts such that not more than 0.05% remains in the finished alloy, in order to obtain sounder castings. Where the alloy is intended for use in a brazing operation such as described above, it has been found essential that the alloy be free of interfering metals, particularly in cases where no added salt flux is utilized. In such use, the presence of appreciable amounts, for example, 0.1% or more, of metals such manganese, aluminum, silicon, and nickel have been found to be deleterious to the resulting brazed joint. These metals, as well as others such as chromium, magnesium, tin, beryllium, vanadium, titanium, and zirconium, tend to produce a resistant surface film on contact at elevated temperatures with gases containing oxygen or oxygenated compounds, such as water vapor or carbon dioxide, which affects the strength of the brazed joint adversely by preventing the desired extent of spreading and bonding of the brazing alloy, and should therefore be avoided.

Alloy compositions in accordance with this invention may be produced in a variety of forms such as sheet, coil, plate, strip, rod and tube. The sheets are readily adapted for forming by the various fabrication methods, for example they may be drawn, spun, formed, and bent. Also, the novel alloys are suitable for treatment by the known plating, tinning, welding, soldering, and brazing methods.

This invention accordingly provides novel alloys of high copper content having improved physical properties, and characterized by a unique resistance to change in such properties when heated. While the invention has been described in the foregoing with particular reference to specific examples, it will be understood that these are illustrative, since it will be realized that variations may be made within the spirit and scope of the invention, as expressed in the appended claims.

Having now described the invention, what is claimed as new and is desired to be secured by Letters Patent, is:

1. An alloy composed of 80% to 95% copper, a proportion of iron not less than a minimum increasing linearly with copper content from 1.25% iron at 80% copper to 2% iron at 95% copper, and the balance 1% to 18.75% zinc.

2. An alloy composed of 80% to 95% copper; an amount of iron between a minimum, which increases linearly with copper content from 1.25% iron at 80% copper to 2% iron at 95% copper, and a maximum 2% greater than the said minimum; and the balance 1% to 18.75% zinc.

3. An alloy composed of 80% to 95% copper, 2% to 2.5% iron, and the balance 2.5% to 18% substantially all zinc.

4. A copper base alloy comprising 5.5% to 8% zinc, 2% to 2.5% iron, and balance copper.

5. A copper base alloy comprising 80% to 95% copper, 1.25% to about 4% iron, and balance 1% to 18.75% substantially all zinc, said alloy being characterized by increased tensile strength and superior resistance to change in physical properties on heating as compared with the iron-free alloy and having a content of less than 0.1% of metals tending to form a resistant surface film on contact with a heated oxidizing gas.

6. A copper base alloy comprising 80% to 95% copper, 2% to 2.5% iron, and balance 2.5% to 18% substantially all zinc, said alloy being characterized by increased tensile strength and superior resistance to change in physical properties on heating as compared with the iron-free alloy and having a content of less than 0.1% of metals tending to form a resistant surface film on contact with a heated oxidizing gas.

7. A copper base alloy comprising 90% to 92% copper, 2% to 2.5% iron, and balance 5.5% to 8% substantially all zinc, said alloy being characterized by increased tensile strength and superior resistance to change in physical properties on heating as compared with the iron-free alloy and having a content of less than 0.1% of metals tending to form a resistant surface film on contact with a heated oxidizing gas.

EDMUND G. MITCHELL.

CERTIFICATE OF CORRECTION.

Patent No. 2,295,180. September 8, 1942.

EDMUND G. MITCHELL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 1, for "balanced" read --balance--; and Table 2, fifth column thereof, for "22" read --33--; page 3, Table 3, in the heading to the fifth column of figures, for "850°" read --800°--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of October, A. D. 1942.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)