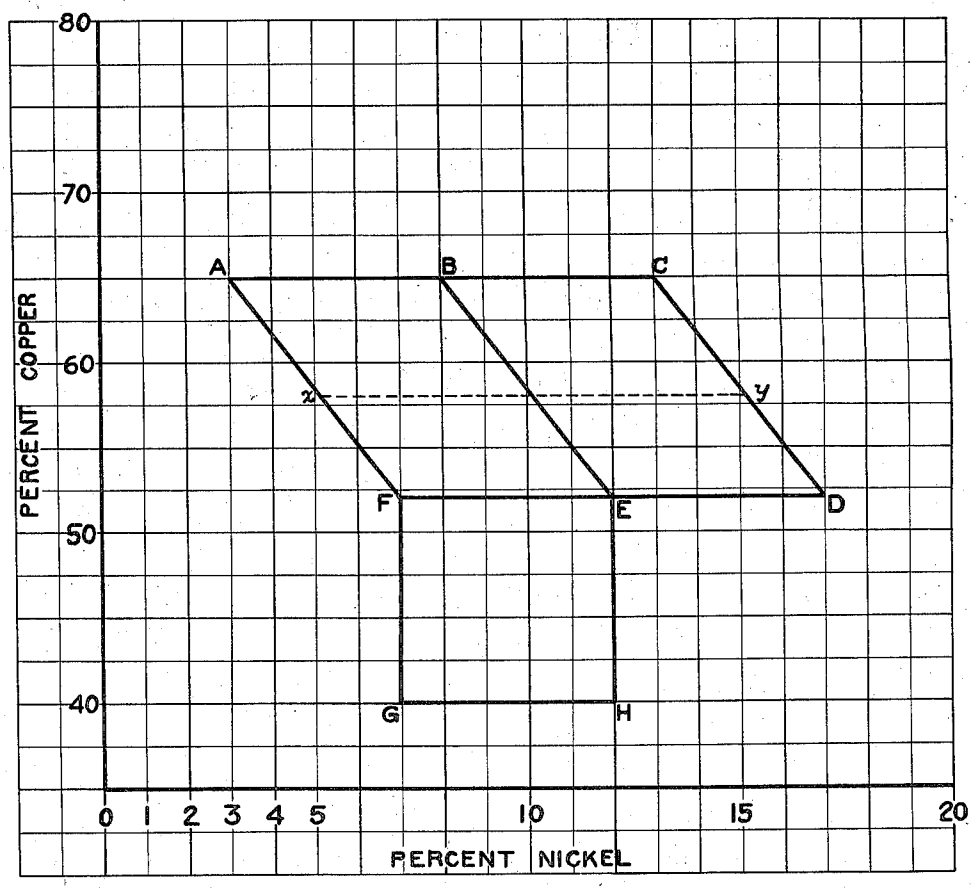
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HOT WORKABLE COPPER ALLOYS

Filed July 13, 1937

COPPER NICKEL ALUMINUM ZINC ALLOYS

Maximum and Minimum Copper Content for Alloys Containing 0.5 to 3% Aluminum with Nickel as Indicated and Remainder Zinc Plus Impurities.



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HOT WORKABLE COPPER ALLOYS

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This invention relates to an improvement in non-ferrous alloys and particularly to an alloy whose principal constituent is copper plus various amounts of nickel and zinc, accompanied in the present invention by small but essential amounts of aluminum, whereby increased strength, resistance to corrosive attack, improved workability and other valuable characteristics are secured. This application is a continuation in part of my prior application Serial No. 750,019, filed October 25, 1934,

Alloys have been made heretofore consisting essentially of copper, nickel and zinc, commonly called "nickel silver", "German silver" etc., and are in general use because of their valuable properties.

This application is directed to the improvement of commercial alloys containing 22% to 53% zinc, 3% to 17% nickel, 40% to 65% copper; and in which the copper is decreased in the range 65% to 52% as the nickel is increased from the range 3% to 13% to the range 7% to 17% nickel; (in other words if we decrease the copper from 65% to 52% the minimum nickel must be increased from 3% at 65% copper up to 7% at 52% copper, and the maximum nickel content increases from 13% at 65% copper to 17% at 52% copper) and with from 52% to 40% copper the nickel content is limited to the range 7% to 12%.

Some of these alloys, namely those with from about 58% to about 65% copper, about 3% to 15% nickel and remainder zinc plus impurities are single phase type (alpha solid solution) when heated to temperatures ranging from about 600° C. to about 900° C. and quenched. Other commercial alloys in the aforementioned range namely those containing from about 52% to about 58% copper, about 5% to 17% nickel have a duplex structure composed of alpha and beta particles. The remainder of the commercial alloys mentioned herein contain from about 40% to about 52% copper, about 7% to about 12% nickel and balance zinc plus impurities and are composed almost entirely of beta phase particles at all temperatures.

I have discovered that when small amounts of aluminum (from about 0.5% to about 3%) are added to the aforementioned "nickel silver" alloys, new and valuable characteristics are obtained not heretofore found in said alloys. This addition of aluminum in amounts from 0.5% to 3% to the copper-nickel-zinc alloys above noted containing about 58% to 65% copper, 3% to 15% nickel, and remainder zinc plus impurities, effects a change from the single phase alpha solid solution, formerly noted in these alloys, to a duplex structure containing alpha plus beta when heated in the annealing temperature range between about 600° C. to approximately 900° C. This is shown by area AC*yx* on the drawing, the line *xy* representing approximately the alpha plus beta boundary for the ternary copper-nickel-zinc alloys. The line AC represents approximately the alpha plus beta boundary line for these alloys containing aluminum in the amounts mentioned. The presence of beta phase particles within the former alpha solid solution range is of considerable significance because it renders the alloys readily susceptible to hot working.

It is generally known that most copper base alloys that contain beta particles can be readily and easily hot worked, whereas the alpha single phase type alloys are not so easily hot worked, if at all. The addition of small amounts of aluminum within the range noted renders that portion of the alpha range extending from about 58% to about 65% copper, from about 3% to about 15% nickel and remainder zinc plus impurities, suitable for hot working such as forging, rolling and extruding at temperatures ranging from about 650° C. to 900° C.

These new alloys, which from other considerations appear logical commercial ones, can be readily hot rolled, hot pressed, forged and extruded, indicating that they can be economically produced. Many of these alloys (those containing from 52% to 65% copper) can also be cold worked sufficiently to provide a smooth surface and some measure of work hardening or temper.

The accompanying drawing which forms a part of this specification shows the range of alloys involved in the invention of this application. This graph is divided into three parts or zones that are thus described.

The area bounded by lines ABEF indicates the best hot and cold working range. It has been found that alloys within these composition limits may be readily and easily hot worked and/or can be reduced by cold working up to about 50%. The composition limits of these alloys are

	Percent
Copper	52 –65
Nickel	3 –12
Aluminum	0.5– 3
Zinc	24 –40.5

and in which the nickel is increased from the range 3% to 8% at 65% copper to the range 7% to 12% at 52% copper as the copper is decreased from 65% to 52%. (In other words if we decrease the copper from 65% to 52% the minimum nickel must be increased from 3% at 65% copper to 7% at 52% copper and the maximum nickel increased from 8% at 65% copper to 12% at 52% copper.)

The area bounded by the lines BCDE indicates the second range wherein the alloys may be satisfactorily hot and cold worked. Working of these alloys and especially those alloys richer

in nickel and/or aluminum, is not so readily or easily accomplished as with the alloys in the first zone. However, the alloys in this second zone are suitable for some commercial purposes.

The limits for this second zone are:

	Percent
Copper	52 –65
Nickel	8 –17
Aluminum	.5– 3
Zinc	19 –35.5

and in which the nickel is increased from the range 8% to 13% at 65% copper to the range 12% to 17% at 52% copper as the copper is decreased from 65% to 52%. (In other words if we decrease the copper from 65% to 52% the minimum nickel must be increased from 8% at 65% copper to 12% at 52% copper, and the maximum nickel increased from 13% at 65% copper to 17% at 52% copper.)

The area bounded by the lines EHGF indicates the third range or extrusion zone wherein the alloys may be readily and easily extruded, forged, pressed or rolled at a red heat but cannot be cold worked to any commercial extent.

The limits for the third zone are:

	Percent
Copper	40 –52
Nickel	7 –12
Aluminum	0.5– 3
Zinc	33 –52.5

These alloys are especially suitable for the production of extruded shapes and hot pressed parts. It should be noted that these limits are not absolute. That is to say there is no sharply defined line that may be drawn between the three ranges, especially between zones 1 and 2. I have found that the characteristics of these alloys gradually change but for commercial practice the zones as drawn delineate the preferred alloys satisfactorily.

The overall composition range, as indicated in the graph, is given as

	Percent
Copper	40 –65
Nickel	3 –17
Aluminum	0.5– 3
Zinc (plus impurities)	19 –52.5 (remainder)

and in which the copper is decreased in the range 65% to 52% as the nickel is increased from the range 3% to 13% to the range 7% to 17% nickel, (in other words if we decrease the copper from 65% to 52% the minimum nickel must be increased from 3% at 65% copper up to 7% at 52% copper, and the maximum nickel content increases from 13% at 65% copper to 17% at 52% copper), and with from 52% to 40% copper the nickel content is limited to the range 7% to 12%.

As an example of intermediate alloys we can take those indicated by dotted line *xy* which shows the minimum nickel at 58% copper is about 5.25% and the maximum nickel is about 15.25%.

Some of these new alloys may be hardened to a limited extent by a low temperature heat treatment after heating to 750° C. to 900° C. and quenching with or without a limited amount of cold working as hereinafter noted, and especially those alloys that are least removed from the alpha boundary (at about 65% copper). On the other hand the alloys containing a larger amount of aluminum and also those with less than about 52% copper do not respond appreciably to hardening by low temperature heat treatment. Likewise no appreciable increase in hardness is obtained after low temperature heat treatment with these alloys when the metal has been reduced about 50% by cold working. That is to say those alloys in the zones ABEF and BCDE can be hardened to a limited extent by low temperature heat treatment.

The maximum hardening temperature for the several annealed alloys, in general, gradually increases as the nickel and/or aluminum is increased from about 400° C. to about 600° C.

The minimum age hardening effect for any of these alloys is obtained when the aluminum content approaches the maximum at 3% and/or when the material has been reduced as much as 50% by cold working. An example, which shows the effect of cold working on the heat hardenability of these alloys is now given. An alloy composed of about 63% copper, 5% nickel, 1% aluminum and 31% zinc that had been reduced about 50% by cold rolling showed a Rockwell "B" hardness of 100 (B scale=$\frac{1}{16}$" ball, 100 kg. load). After being heat treated in an electric muffle furnace at approximately 500° C. the hardness value of this same sample was found to be 101. When the said alloy was annealed at approximately 775° C. for two hours and quenched the hardness value was 63, which after the specimen was heat treated for two hours at 500° C. was raised to B 80.

Another example which shows the effect of increased amounts of aluminum in preventing age hardening is now given. An alloy composed of about 63% copper, 5% nickel, 3% aluminum and 29% zinc that had been reduced about 50% by cold rolling showed a Rockwell B hardness value of 99. After being heat treated in an electric muffle furnace for two hours at approximately 500° C. the hardness value of this same sample was 93. When the said alloy was annealed at approximately 775° C. for two hours and quenched the "B" hardness value was 81, which after the specimen was heat treated for two hours at about 500° C., was still 81, indicating little or no increase in hardness when heated at a low temperature.

A further advantage of some of the alloys made in accordance with the present invention is the increase in tensile strength which is obtained by heat treatment at low temperatures. This increase in strength is also accompanied by an increase in elongation. All of the previously mentioned commercial copper-nickel-zinc alloys (paragraph 3, page 1) are not capable of being successfully strengthened or hardened by heat treatment at low temperatures.

Articles may be fabricated from the annealed or wrought alloy, and when finished may be hardened to a limited extent by low temperature heat treatment. The resistance of these new alloys to corrosive attack is superior to that of the previously mentioned ternary commercial alloys.

There are other advantages secured by the addition of aluminum to these alloys. Thus for example loss of zinc during casting is reduced by the protective film produced by the aluminum on the metal. Also, the color effect is maintained by the aluminum addition so that it is possible to reduce the nickel about one or two percent without loss of proper color, and thus reduce the cost of the alloy.

With the aluminum addition pickling is more or less unnecessary for heavy gauges, and there is no heavy scale with thin gauge metal.

In short these new alloys are suitable for the operations and uses peculiar to the brass and copper industries.

To total one hundred percent the "remainder" in the range above noted is more advantageously zinc, but in practice elements other than zinc may be present in slight amounts without injury to the resultant product. Thus, for example, it is common practice to add a small amount of manganese to copper-nickel-zinc alloys and this metal (up to 0.5%) may be added to my alloy. Because it cannot be avoided without too much expense in refining the constituent metals, there may be and usually are some lead and iron present.

In view of the fact that my improvement applies to a great number of copper-nickel-zinc-aluminum alloys, it is impossible to state all of the commercially useful alloys in the group. However, for informative purposes I am listing a few of the most important alloys which because of my invention are a great improvement over the mentioned copper-nickel-zinc alloys.

Copper	Nickel	Aluminum	Zinc
63	5	1	31
63	12	1	24
60	8	1	31
60	8	2	30
60	12	1	27
60	12	2	26
55	10	1	34
55	15	1	29
50	8	1	41
46	10	1	43
46	10	2	42
42	10	1	47

These improved alloys containing more than 52% copper that have been work hardened by drawing or rolling can be softened somewhat by annealing at about 800° C. and quenching in cold water, and, if desired, can again be hardened by cold working. The annealed or work hardened metal, whether in the form of sheet, rod, tube, etc. can be readily fabricated into the finished product and then hardened somewhat by heat treatment at a low temperature. This hardening by low temperature heat treatment after fabrication is suitable for such articles as nuts, bolts, nipples, valves, keys, clock parts, and the like.

They have also been found to be corrosion resistant and characterized by the presence of a protective surface film, and some of the alloys can be hardened by heat treatment at low temperatures (approximately 300° C. to 600° C. for periods of about two hours or less), but they can also be hardened by heat treating for longer periods of time at lower temperatures (150° C. to 300° C.).

These new alloys containing aluminum are particularly satisfactory for certain uses when not hardened by low temperature heat treatment as their resistance to corrosive attack is considerably better than that of the alloys without the aluminum. They also have good strength and elongation and can be fabricated into various articles.

These alloys are also useful for welding and for welding rods, and may be brazed. In addition to their workability and adaptability to be forged, pressed and extruded some of the alloys, namely those containing more than 52% copper, may be drawn into rods, wire, tubes, sheets and shapes, and other metal articles.

Having thus set forth the nature of my invention, what I claim is:

1. An alloy composed of copper, nickel, zinc and aluminum in proportions within the following ranges,

	Percent
Copper	40 to 65
Nickel	3 to 17
Aluminum	0.5 to 3
Zinc (plus impurities)	19 to 52.5

and in which as the copper is decreased from 65% to 52% the minimum nickel is increased from 3% at 65% copper up to 7% at 52% copper and the maximum nickel content increases from 13% at 65% copper to 17% at 52% copper; and with from 52% to 40% copper the nickel content is limited to the range 7% to 12%.

2. An alloy characterized by being workable hot and cold composed of copper, nickel, zinc and aluminum in proportions within the following ranges,

	Percent
Copper	52 to 65
Nickel	3 to 12
Aluminum	0.5 to 3
Zinc (plus impurities)	24 to 40.5

and in which the nickel is increased from the range 3% to 8% at 65% copper to the range 7% to 12% at 52% copper as the copper is decreased from 65% to 52%.

3. An alloy characterized by being workable hot and cold composed of copper, nickel, zinc and aluminum in proportions within the following ranges,

	Percent
Copper	52 to 65
Nickel	3 to 17
Aluminum	0.5 to 3
Zinc (plus impurities)	19 to 40.5

and in which the nickel is increased from the range 3% to 13% at 65% copper to the range 7% to 17% at 52% copper as the copper is decreased from 65% to 52%.

4. An alloy characterized by being hot workable composed of copper, nickel, aluminum and zinc in proportions within the following ranges,

	Percent
Copper	40 to 52
Nickel	7 to 12
Aluminum	0.5 to 3
Zinc (plus impurities)	33 to 52.5

5. An alloy composed of approximately 63% copper, 5% nickel, 1% aluminum, and zinc remainder.

6. An alloy composed of approximately 60% copper, 8% nickel, 2% aluminum, and zinc remainder.

7. An alloy composed of approximately 42% copper, 10% nickel, 1% aluminum, and zinc remainder.

8. A heat hardened and strengthened copper alloy composed of copper, nickel, aluminum and zinc in proportions within the following ranges,

	Percent
Copper	52 to 65
Nickel	3 to 17
Aluminum	0.5 to 3
Zinc (plus impurities)	19 to 40.5

and in which the nickel is increased from the range 3% to 13% at 65% copper to the range 7% to 17% at 52% copper as the copper is decreased from 65% to 52%.

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