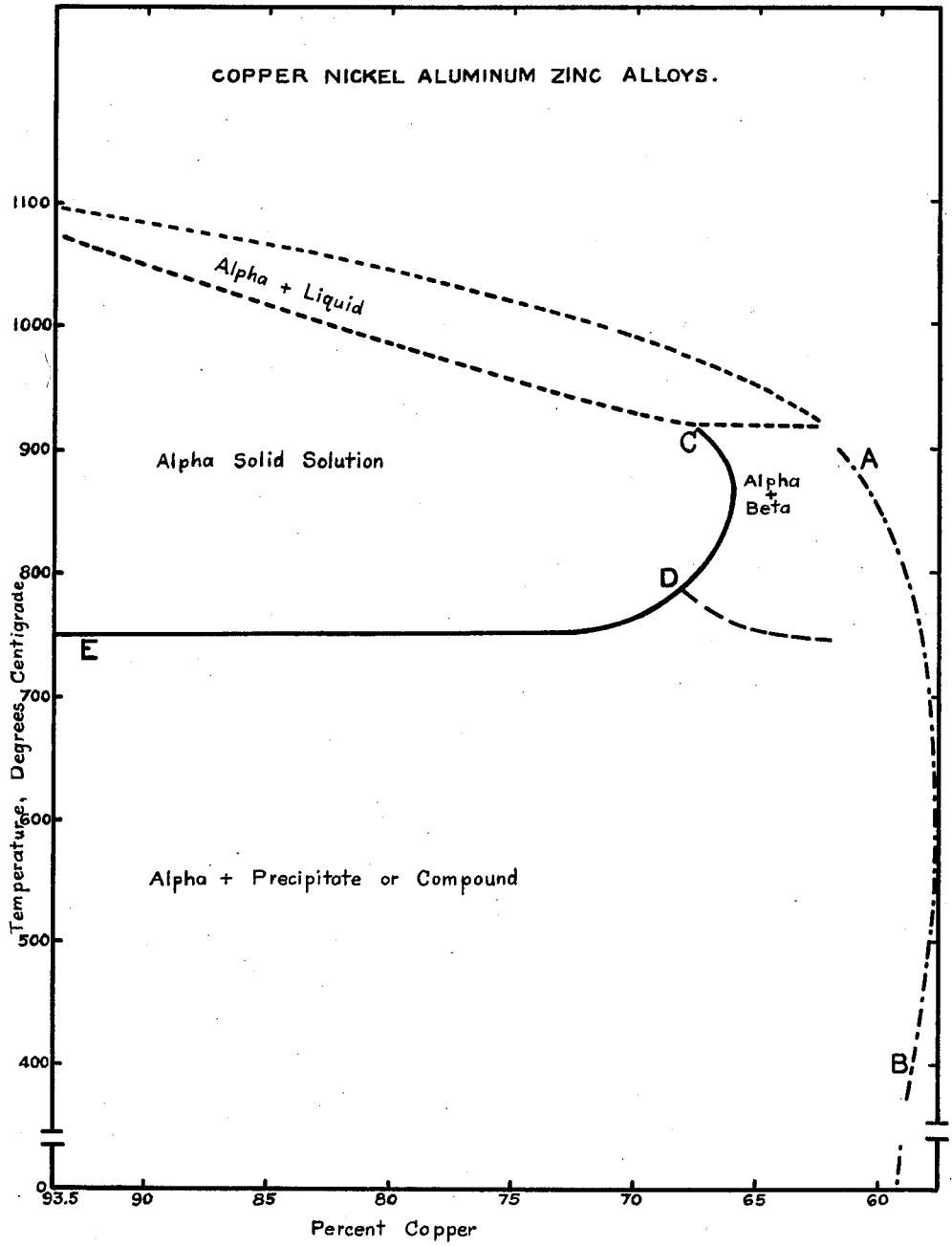
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COPPER BASE ALLOY

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Section of the Quaternary Copper Nickel Aluminum Zinc Diagram at 5% Nickel and 1.5% Aluminum.

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COPPER BASE ALLOY

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10 Claims. (Cl. 75—155)

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.

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. The composition range of these commercial alloys is

	Per cent
Copper	56 to 93
Nickel	3.0 to 30
Zinc	Remainder (4 to 41)

but the present invention relates to those alloys which are single phase type when heated to the neighborhood of 850° C. and quenched, these alloys containing 66% to 95.5% copper.

I have discovered that when small amounts of aluminum (from about 0.5% to about 4%) are added to the single phase type (alpha solid solution) copper-nickel-zinc alloys, new and valuable characteristics are obtained not heretofore found in said alloys.

The effect of adding aluminum to these copper-nickel-zinc alloys is shown in the drawing which is a section of the quaternary copper-nickel-aluminum-zinc diagram at 5% nickel and 1.5% aluminum. The phase boundary line separating the alpha and alpha plus beta fields however is considerably affected by the addition of aluminum in amounts up to about 4%. This effect may be seen by observing the position of line AB for the ternary alloy in which the beta constituent is not present in alloys containing more than about 62% copper whereas for a similar alloy containing 1.5% aluminum the boundary line is moved to the left to approximately 66% copper as shown by line CD. Likewise there is a phase change when there is materially more than about 4% aluminum present in the alloy, and with aluminum contents above about this percent we again have a duplex structure.

This boundary at 66% copper is of considerable importance because it differentiates between the annealed alpha solid solution alloys and the duplex type phases such as alpha plus beta, alpha plus delta et al., which provide entirely different characteristics. For example I have found that copper-nickel-aluminum-zinc alloys containing up to about 20% nickel and less than 66% copper have a duplex phase structure and show a considerable decrease in corrosion resistance at normal and elevated temperatures as compared with the alpha alloys, can be cold worked to a limited extent only, have distinct mechanical properties as indicated by tensile strength, hardness, elongation, etc. and cannot be hardened by low temperature heat treatment to as great an extent as those containing all alpha solid solution. In other words at about 66% copper there are distinct changes in characteristics which materially affect commercial applications. Thus it is noted that there is a definite change in characteristics when the copper content is less than 66% in these quaternary alloys.

In the ternary system of the copper-nickel-zinc alloy the alpha plus beta phase boundary is the dot and dash line AB, as shown by the diagram of Hansen and Bauer, Zeit. fur Met. November, 1929, but with the addition of 1.5% aluminum it is the solid line CD and a new phase boundary appears within the former alpha solid solution field shown by the line DE. This line very closely represents the maximum temperature at which the new hardening constituent may be present in the alloy. In other words at temperatures below this line the structure is composed of alpha plus precipitate or compound. At temperatures above 600° C. and up to about 750° C. the hardening constituent coalesces to such a degree that the precipitate or compound is rendered less effective as a hardening agent. The preferred hardening range extends from about 400° C. to about 600° C. for periods of about two hours. Below 400° C. some hardening occurs in this length of time, but the precipitate is more or less submicroscopic and greater hardening may be secured by heating for longer periods. The maximum hardening temperature for the several annealed alloys in general gradually increases as the nickel or aluminum is increased from about 400° C. to about 600° C., and for work hardened alloys from about 450° C. to about 650° C.

With variations in the aluminum content within the range of 0.5% to 4% the phase boundary line DE for a given nickel content is not greatly affected. Microscopic examination of the precipitate or compound formed with heat treatment from 400° C. to 600° C. reveals that the particle size of the same is very minute and considerably smaller than that observed in several other

known precipitation hardening alloys. This may account for the satisfactory elongation and corresponding high strength obtained with the present alloy.

An alloy or alloys made in accordance with the present invention are suitable for the same uses as the prior, or previously commonly used copper-nickel-zinc alloys, and in addition have several new uses hereinafter mentioned. A considerable improvement in corrosion resistance, and especially resistance to oxidation at all temperatures below 500° C. is obtained with my improved alloy or alloys.

A very important advantage of an alloy embodying the essential features of the present invention is the great increase in hardness that may be obtained by heat treatment at low temperatures. For example, an alloy composed of about 69% copper, 5% nickel, 24.5% zinc and 1.5% aluminum that had been cold rolled from 0.031" gauge to 0.040" gauge sheet has a Rockwell "G" hardness value of 72, (G scale=$\frac{1}{16}$" ball, 150 kg. load). After being heat treated in an electric muffle furnace for 2 hours at approximately 400° C., the hardness value of this same sample is increased to 84. After the said alloy has been annealed at approximately 825° C. for 1 hour and quenched, the "G" hardness value is minus 22, which, after the specimen is heat treated for 2 hours at about 450° C., is raised to "G" 73. The prior copper-nickel-zinc alloys are not capable of being successfully hardened by heat treatment at low temperatures. The importance of this age hardening or precipitation hardening is readily apparent. Articles may be fabricated from the annealed or wrought alloy, and when finished may be hardened by low temperature heat treatment. Because the alloy is not susceptible to softening at temperatures up to about 500° C., it is suitable for condenser tubes, parts for internal combustion engines and other uses subject to operating temperatures below 500° C. The resistance of this alloy to wear, when hardened, is noteworthy.

A further advantage of an alloy or alloys made in accordance with the present invention is the great increase in tensile strength which is obtained by heat treatment at low temperatures. This increase in strength, is accompanied by unusual effect, namely an increase in elongation. This increase in elongation means an increase in ductility and indicates greater resistance to fatigue of the hardened alloy made according to my invention as opposed to low percentage elongation or brittleness which is found in some age hardened alloys.

After annealing my improved alloys, the presence of a greenish gray film was noted on the surface of the metal. Most of this film was removed by immersion in dilute sulphuric acid followed by a thorough rinse in water and a wipe with cotton cloth. After drying, the presence of a very thin, dull, gray film was again noted on the surface of the metal. This film appears to afford some protection against intercrystalline attack and corrosion.

These improved alloys containing aluminum have shown very good resistance to attack by corrosion when immersed in concentrated and dilute nitric acid at room temperature and at 86° C. I have also found that the resistance of these alloys to corrosive attack by several other oxidizing agents is increased considerably.

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. Overhauling is very light as it is required to remove surface only. Pot annealing is unnecessary.

In short these new alloys are suitable for the operations and uses peculiar to the brass and copper industries. Thus for example they are adapted for cold rolling and drawing, as well as drawing into shells, cartridge cases and wire.

I am aware that a patent has been granted to Price No. 1,815,071, for a copper-nickel-aluminum-zinc alloy containing preferably 80% copper, 2% aluminum, 1% nickel, the remainder being substantially zinc. The maximum amount of nickel in the claim is 2½%. I have found the disclosure of that patent worthless for the purpose of obtaining a commercial age hardenable alloy or one that is hardenable to an appreciable extent, or an alloy that is resistant to softening at elevated temperatures together with other advantages mentioned herein. Price stated in a booklet entitled "Alcunic Condenser Tubing" that he had not succeeded in hardening the alloy by reheating after quenching from a higher temperature. My experiments have shown that at least approximately 3% nickel must be present and in addition 0.5% or more aluminum to obtain an alloy which can be appreciably hardened by heat treatment at low temperatures. Consequently, my invention requires the presence of more than 2½% nickel for commercial application and does not conflict with the alloy of the Price patent.

I have found that the improvements and advantages noted are secured in aloys comprising as essential ingredients copper, nickel, aluminum and zinc, within ranges of approximately the following.

Copper	percent	66.0 to 95.5
Nickel	do	3 to 30
Aluminum	do	0.5 to 4
Zinc	Remainder (plus impurities)	

To total one hundred percent the "difference" is most 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 1%) 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. Tin in amounts up to 2.12% was added to this improved alloy but no further improvement was obtained. The great increase in hardness is only obtained when nickel and aluminum are present together in the alloy and when the nickel content is at least 3.0 percent. If the aluminum is omitted, no material hardening is obtained by heat treatment at low temperatures.

The nickel content must exceed the aluminum content to obtain the maximum hardness for the alloy. The indications are that a very satisfactory ratio is at least about 3 to 1.

In view of the fact that my improvement applies to a great number of commercially produced

copper-nickel-zinc 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 have been greatly improved by my invention.

Nickel	Aluminum	Copper	Zinc
4	1	93	Remainder.
5	1.5	70	Do.
6	2	90	Do.
10	1.5	68	Do.
10	3	75	Do.
10	3	85	Do.
12	3	80	Do.
15	1.5	68	Do.
20	1.5	67	Do.
30	1	67	Do.

Improved alloys of this type containing more than 66% copper that have been work hardened by drawing or rolling can be softened by annealing at about 825° C. and quenching in cold water. They can also be work hardened after annealing and quenching. The annealed or work hardened metal, whether in the form of sheet, rod, tube, et al., can be readily fabricated into the finished product and then hardened by heat treatment at a low temperature. It can if desired be further work hardened after the low temperature heat treatment. This hardening by low temperature heat treatment after fabrication is especially suitable for such articles as nuts, bolts, fuse bodies, primers, nipples, valves, springs, wire screens, hinges, chains, jewelry, tableware, coins, 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 can be hardened by heat treatment at low temperatures (approximately 300° C. to 525° 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.

These new alloys are also very satisfactory for certain uses when not hardened by low temperature heat treatment as they are corrosion resistant, have good strength and elongation and can be readily fabricated into various articles.

The alloy is also useful for welding and for welding rods, and may be brazed. In addition to its workability and adaptability to be drawn into wire as previously noted it may be drawn into rods, tubes, sheets and shapes, and also drawn, stamped or spun into cups, cartridge cases 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	66 to 95.5
Nickel	3 to 30
Aluminum	0.5 to 4
Zinc	1 to 30.5

2. An alloy composed of 66% to 95.5% copper, 3% to 30% nickel, 0.5% to 4% aluminum, and 1% to 30.5% zinc, and in which the nickel content exceeds the aluminum content.

3. A copper base alloy composed of from 66% to 95.5% copper, 3% to 30% nickel, 0.5% to 4% aluminum, and 1% to 30.5% zinc, and in which the content of nickel is at least three times that of aluminum.

4. An alloy characterized by being hardenable and increased in strength by heat treatment at low temperatures, being resistant to softening at elevated temperatures, and resistant to corrosion and oxidation at temperatures below 500° C., composed of copper, nickel, zinc and aluminum in proportions within the following ranges:

	Percent
Copper	66 to 95.5
Nickel	3 to 30
Aluminum	0.5 to 4
Zinc	1 to 30.5

5. An alloy characterized by being hardenable and increased in strength by heat treatment at low temperatures, being resistant to softening at elevated temperatures, and resistant to corrosion and oxidation at temperatures below 500° C., composed of 66% to 95.5% copper, 3% to 30% nickel, 0.5% to 4% aluminum, and 1% to 30.5% zinc, and in which the nickel content exceeds the aluminum content.

6. An alloy characterized by being hardenable and increased in strength when utilized at temperatures above room temperature up to 500° C. composed of 66% to 95.5% copper, 3% to 30% nickel, 0.5% to 4% aluminum, and 1% to 30.5% zinc, and in which the nickel content exceeds the aluminum content.

7. An alloy composed of approximately 70% copper, 5% nickel, 1.5% aluminum, and balance zinc.

8. An alloy composed of approximately 68% copper, 10% nickel, 1.5% aluminum, and balance zinc.

9. An alloy composed of approximately 67% copper, 20% nickel, 1.5% aluminum, and balance zinc.

10. A heat hardened copper base alloy composed of 66% to 95.5% copper, 3% to 30% nickel, 0.5% to 4% aluminum, and balance zinc.

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