United States Patent

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[54] **TWO PHASE NICKEL-ZINC ALLOY**
9 Claims, 3 Drawing Figs.

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[50] **Field of Search** .... 148/11.5, 12.7, 32, 160; 75/157.5, 170, 178 R, 178 C

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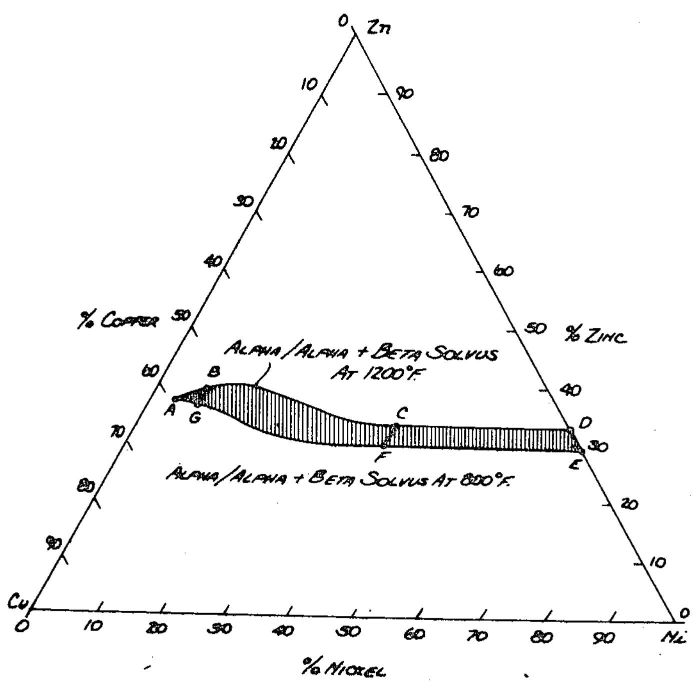
ABSTRACT: Process of heat treating and mechanically working nickel-zinc alloys or copper-nickel-zinc alloys produces products having special alpha-beta microstructure characterized by high strength at room temperature and high deformability at elevated temperatures.



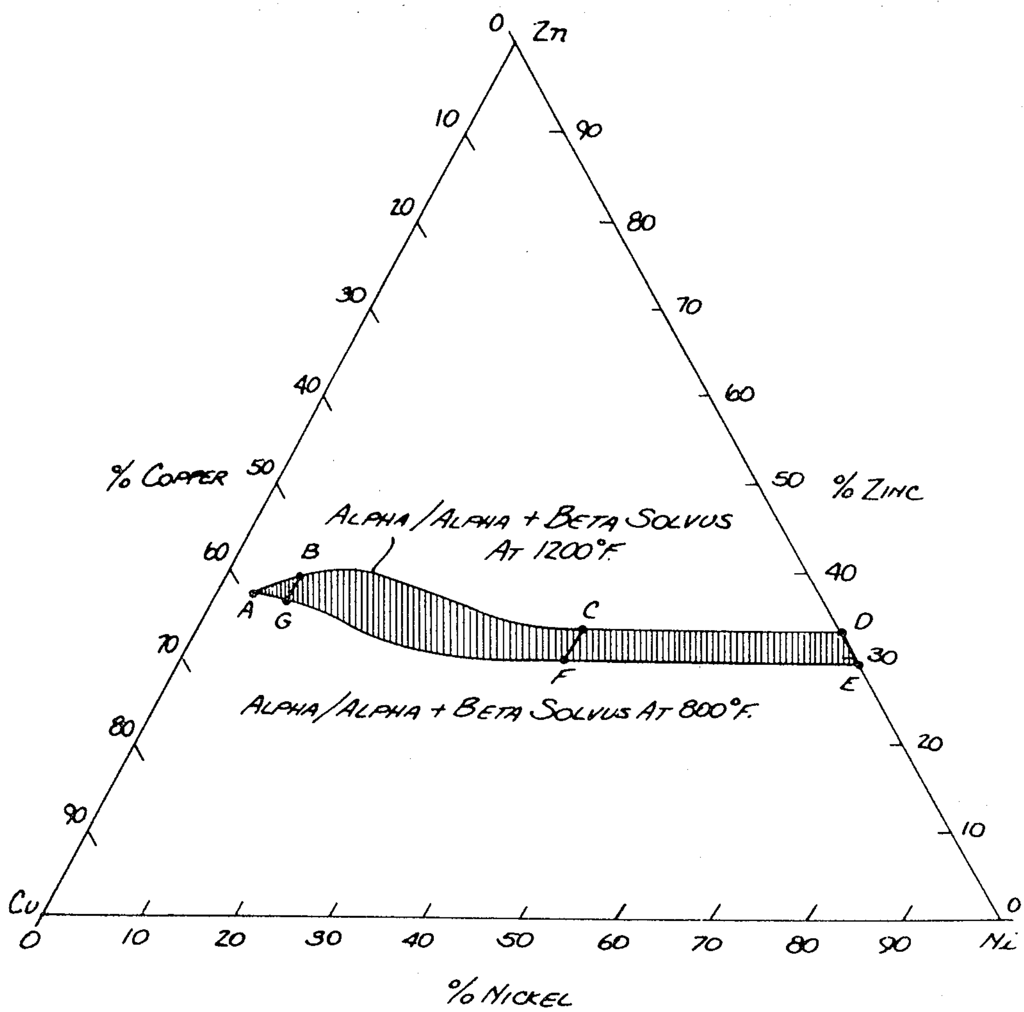


Fig. 1.

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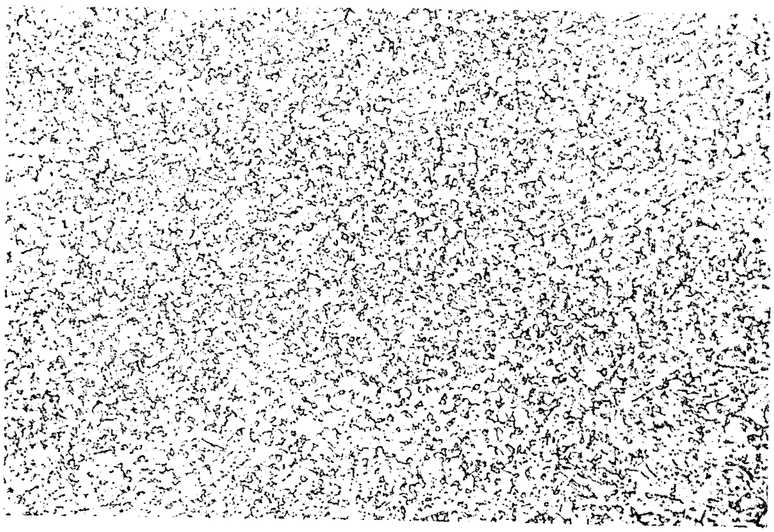

FIG. 2

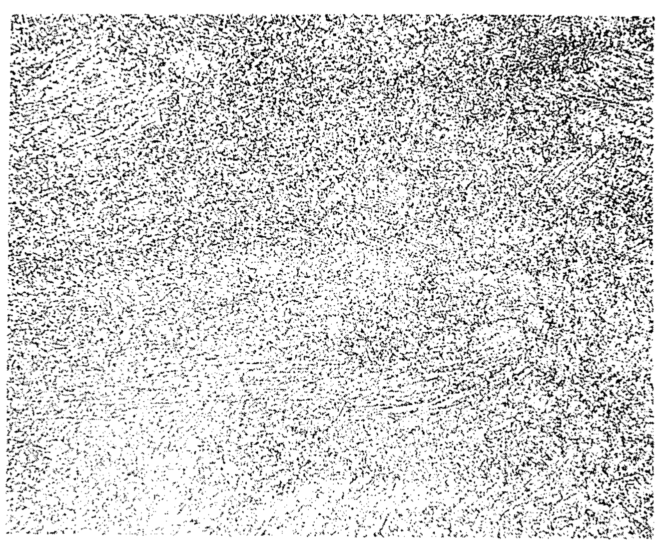

FIG. 3

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TWO PHASE NICKEL-ZINC ALLOY

The present application is a division of our copending U.S. application Ser. No. 13,913, filed Oct. 14, 1969.

The present invention relates to metallurgy of alloys in the copper-nickel-zinc ternary system, including certain nickel-zinc alloys at the boundary of the copper-nickel-zinc system, and more particularly relates to thermomechanical processing of copper-nickel-zinc alloys and to wrought copper-nickel-zinc alloy products.

A variety of copper-nickel-zinc alloys have been known for at least several centuries and have been known to possess various desirable combinations of malleability, mechanical characteristics (including strength and ductility) and general corrosion resistance. Many metallurgical studies of the copper-nickel-zinc system have been reported in the art and certain metallurgical phases in this system, e.g., the face-centered cubic alpha and several beta-type phases including body-centered cubic beta and body-centered tetragonal beta types, are well known. Some of the alloys which have a rich white (silverlike) color are known as nickel silvers or German silvers and both single-phase alpha nickel silvers and dual phased alpha-beta nickel silvers are known. While the term nickel silver usually refers to alloys containing about 9 percent to about 20 percent or 25 percent nickel it is known that the alpha and beta phases are also obtained in copper-nickel-zinc alloys with much more nickel, e.g., 40 percent or 60 percent nickel, and even in alloys containing about 71 percent nickel along with about 29 percent zinc in which very little or no copper is present.

While known copper-nickel-zinc alloys have been used in many articles, including tableware, medical instruments, scientific measuring instruments and electric switches, it has long been desirable to obtain improved combinations of strength and ductility characteristics with these alloys. It has been known that tensile strength, including ultimate tensile strength and yield strength, can be increased by simply cold working the alloys. However the strength increases obtained by cold working have been accompanied by serious reductions in ductility, particularly tensile elongation. Furthermore, even when tensile strength has been increased by cold working, fatigue strength characteristics have remained undesirably low. Need for high fatigue strength in combination with a high yield strength or elastic limit has been particularly great where the alloy is needed for making vibratory elements and springs.

Tensile strengths can also be increased by addition of other elements, such as aluminum, titanium or columbium, which enable strengthening by age hardening, but age hardening has not satisfied the need for increased fatigue strength and the heat treatment requirements can sometimes introduce manufacturing difficulties.

Another important need has been to obtain highly improved formability in order to enable production of a greater variety of shapes in products. Enhanced formability has been especially desirable for increasing the usefulness of the white colored copper-nickel-zinc alloys inasmuch as the rich silverlike color of these alloys is highly desirable for articles that are both ornamental and utilitarian, e.g., tableware such as cream pitchers and gravy boats. It has been very obvious that improved formability characteristics would provide artists, craftsman and engineers with greater scope for designing to meet esthetic and engineering needs.

Although many attempts were made to overcome the foregoing difficulties and others and provide copper-nickel-zinc alloy products having improved combinations of strength and ductility characteristics, none, as far as we are aware, has fully satisfied all of the outstanding needs.

There has now been discovered a thermomechanical process that provides nickel-zinc, including copper-nickel-zinc, alloy products with new and enhanced characteristics of strength and ductility, including formability, along with good corrosion resistance.

An object of the present invention is to provide a wrought and heat treated nickel-zinc (or copper-nickel-zinc) alloy product having a two-phase microstructure characterized by a

useful combination of strength, ductility and corrosion resistance.

A further object of the invention is to provide a process for working and heat treating nickel-zinc alloys to produce strong, ductile and corrosion resistant products thereof.

Other objects and advantages of the present invention will be apparent from the following description taken in conjunction with the accompanying drawing in which:

FIG. 1 shows an alloy composition diagram pertaining to the copper-nickel-zinc ternary system;

FIG. 2 is a reproduction of a photomicrograph taken at a magnification of 1,000 diameters (1,000X) illustrating the etched two-phase microstructure of an embodiment of the wrought and heat treated product of the invention; and

FIG. 3 is a reproduction of a photomicrograph taken at 500X magnification illustrating the etched two-phase microstructure of another embodiment of the wrought and heat treated product of the invention. The microstructure illustrated by FIG. 2 and FIG. 3 were both produced in accordance with the process of the invention.

Generally speaking, the present invention contemplates a wrought and heat treated product made of a special alloy composition containing zinc and nickel, advantageously 8 percent to 40 percent nickel, and in most instances copper, and having a two-phase microstructure comprising a fine grained alpha matrix with fine beta particles dispersed intergranularly throughout the alpha matrix. Useful room temperature characteristics of the product of the invention particularly include, among other things, high strength that is generally much greater than the normal strengths of conventional copper-nickel-zinc alloys such as nickel silvers, good ductility and formability in combination with the high strength, and generally good corrosion resistance. Additional important characteristics obtained with embodiments of the present product include high fatigue strength at room temperature and extraordinarily high formability at elevated temperatures. The invention also contemplates a thermomechanical metallurgical process, which provides products in accordance with the invention, comprising cold working an alloy of the special nickel-zinc composition in the alpha solid solution condition (the single phase condition) and then, while the alloy possesses strain-energy from the cold work, heat treating the cold-worked single-phase alloy at a temperature at or above the recrystallization temperature and below the alpha/alpha plus beta solvus of the alloy and in the range of about 700° F. to about 1,150° F. to recrystallize the alloy into a fine-grained structure and simultaneously precipitate fine beta particles in an intergranular dispersion throughout the alpha matrix. While the product can also have some beta within the alpha grains, it is to be understood that the beta is dispersed predominately intergranularly.

The special alloy composition of the invention is the range of area of composition in the copper-nickel-zinc ternary system that is characterized by an alpha/alpha-plus-beta solvus temperature of 800° F. to 1,200° F. Thus, the alloy composition is the area of composition bounded (including the boundary) by the 800° F. and 1,200° F. solvus lines and the nickel-zinc (binary) boundary line on the copper-nickel-zinc ternary diagram; this area of composition in accordance with the invention is illustrated by the shaded area bounded by the 1,200° F. solvus line ABCD, the nickel-zinc boundary line DE from about 29 percent to about 33 percent zinc and the 800° F. solvus line EFGA. All alloy composition percentages referred to herein are by weight. The coordinates of the points A through G on the ternary diagram in FIG. 1 are set forth in the following coordinate table.

COORDINATE TABLE

	% Ni	% Zn	% Cu
A	4	37	59

B	8	39	53
C	40	33	27
D	67	33	0
E	71	29	0
F	29 40		31
G	8	36	56

An important area of composition for practical commercial production is bounded by BCFGB.

Where desired, the scope of the shaded area ABCDEFGA which illustrates the composition of the alloy for the process and product can be usefully described to a straight line approximation with minimum and maximum percentages as follows:

	Minimum	Maximum
Nickel:	4%	71%
Zinc:	From 4% to 20% Ni %Zn=39−0.375(%Ni) From 20% to 35% Ni %Zn=34.2−0.133 (%Ni) From 35% to 71% Ni %Zn=29.5	From 4% to 10% Ni %Zn=36+0.415(%Ni) From 10% to 15% Ni %Zn=40 From 15% to 40% Ni %Zn=44.2−0.28 (%Ni) From 40% to 67% Ni %Zn=33
Copper:	Balance	Balance

An advantageous range of composition is included by percentages in accordance with the following:

	Minimum	Maximum
Nickel:	8%	40%
Zinc:	%Zn=38−0.23(%Ni)	%Zn=42−0.23(%Ni)
Copper:	Balance	Balance

While the alloy may be referred to as having a balance of copper or zinc, this does not exclude small amounts of auxiliary elements, such as deoxidizers, desulfurizers, etc., and incidental elements or impurities. Accordingly, the alloy can contain up to about 0.1 percent titanium, up to about 0.03 percent aluminum, up to about 0.5 percent magnesium and up to about 1 percent manganese. Iron, carbon and silicon are undesirable and should be restricted to not more than about 0.15 percent iron, about 0.05 percent carbon and about 0.05 percent silicon and more desirably not more than 0.05 percent, 0.01 percent and 0.01 percent of each, respectively. Elements such as bismuth, phosphorus, sulfur and tellurium can be detrimental and should be limited to not more than 0.005 percent each. Although lead is not required, up to 1 percent or higher, e.g., 2 percent lead can be added to improve machinability. However, where it is desired to obtain especially good formability at elevated temperatures, lead should be controlled to low levels such as up to about 0.05 percent or advantageously not more than 0.015 percent.

In view of the foregoing description pertaining to the alpha/alpha-plus-beta solvus relationships and the shaded area in FIG. 1, it is apparent that the nickel, zinc and any copper in the alloy are within the ranges of about 4 percent to about 71 percent nickel, about 29 percent to about 40 percent zinc and up to about 59 percent copper.

It is also important to note that the controlled composition provides a required cold workability characteristic that enables cold working the alloy into a condition having a recrystallization temperature below the alpha/alpha-plus-beta solvus temperature, advantageously 50° F. to 200° F. below the solvus, of the alloy.

The alpha component of the microstructure referred to herein is the face-centered cubic structured alpha phase in the copper-nickel-zinc system and the beta component is one or more of the beta-type phases which have body-centered cubic or body-centered tetragonal structures in the copper-nickel-zinc system. Finely divided alpha-beta microstructures in accordance with the invention are illustrated (etched with potassium dichromate) by FIGS. 2 and 3 of the accompanying drawing. FIG. 2 shows an especially good, fully recrystallized, balanced two-phase microstructure with equiaxed beta uniformly distributed in a fine-grained alpha matrix in a product of an alloy containing about 10 percent nickel, 38.3 percent zinc and essentially balance copper (about 51.7 percent copper by difference) which was processed by hot extrusion, solution annealing for 1 hour at 1,200° F. and water quenching, thereafter cold rolling to 85 percent reduction, and then recrystallization-precipitation treating for 17 hours at 900° F. followed by air cooling. FIG. 3 shows a marginally acceptable, satisfactory, fine alpha-beta microstructure that is about 80 percent recrystallized (thus predominantly although not completely recrystallized) with some beta not equiaxed in a product which is also of an alloy containing about10 percent nickel, 38.3 percent zinc and balance essentially copper and which was processed by hot extrusion, solution annealing for 1 hour at 1,200° F. and water quenching, cold rolling to 72 percent reduction and recrystallization-precipitation treating for 2 hours at 900° F. followed by air cooling.

The fine alpha-beta microstructure has a fine-grained alpha matrix with average grain size diameter not greater than the order of about 10 microns. It is advantageous that the alpha grain size be not greater than about 5 or 6 microns, such as 1 to 5 microns, in order to obtain uniformly high strength and ductility characteristics and especially good hot formability. The bet particles are generally about the same size or smaller than the alpha grains. The beta is dispersed at the alpha grain boundaries and, importantly, are in finely divided discontinuous pattern and do not form grain boundary networks, films or stringers.

At the start of cold working in the process of the invention, the alloy is in an essentially homogeneous solid-solution condition free from coarse structures, such as coarse dendritic or other segregation or precipitates. Accordingly, where the alloy is prepared by usual procedures of melting and casting into ingot form, the as-cast structure should be well broken up by hot working, e.g., extrusion or forging. Moreover, inasmuch as the alloy usually precipitates beta when normally cooled, for instance, when air cooled in section thicknesses of about one-half inch or greater, it is important that the alloy be solution treated prior to the cold working. Solution treatment to place the alloy in the required solid solution condition can be accomplished by solution annealing the alloy at a temperature above the solvus (alpha/alpha plus beta) for a time sufficient to dissolve any second phase and then cooling the alloy rapidly enough to prevent any diffusion-based reactions, such as precipitation. Advantageously, for solution treatment, the alloy is heated to a temperature of 50° F. to 200° F. above the solvus for about 10 minutes to 2 hours and then cooled in the solid solution condition; when the alloy contains 4 percent to 8 percent to 20 percent nickel, normal air cooling is sufficiently rapid for section thicknesses up to one-half inch, but for thicker sections, or when the alloy contains more than 20 percent nickel, the alloy should be cooled more rapidly such as by water quenching.

With the alloy in the slid solution condition, the alloy is cold worked an amount effective to depress the recrystallization temperature to below the solvus, advantageously at least about 50° F. below the solvus and more advantageously 100° F. to about 200° F. below the solvus. Although in some instances as little as 30 percent cold worked (30 percent reduction in cross secton area) or possibly less may be satisfactory the alloy is advantageously cold worked at least about 60 percent or better, 72 percent or 85 percent, in order to provide sufficient strain energy for recrystallization into a good fine-grained two-phase structure.

Following the cold working, the alloy while in the cold worked, alpha-phase solid solution condition is subjected to a recrystallization-precipitation treatment by heating the cold worked alloy to, and advantageously, above the recrystallization temperature of the alpha phase and yet below the solvus in order to precipitate sufficient beta phase to control the recrystallized alpha grain size. Advantageously, the recrystallization-precipitation treatment is at 50° F. to about 200° F.

below the solvus for a period of one-quarter hour to about 24 hours. The recrystallized and precipitated structure provided by the invention has good stability and, accordingly, the heating time may be longer than 24 hours and the cooling rate may be either fast or slow, e.g., air cooling.

For carrying the invention into practice, an especially advantageous processing cycle, especially for alloys containing 8 percent to 40 percent nickel, is to solution treat the alloy by heating at 1,150° F. to 1,300° F. for 30 minutes to 2 hours and thereafter water quenching, or air cooling if the alloy contains 20 percent or less, e.g., 18 percent, nickel, cold working the solution treated alloy at least about 80 percent and then heat treating the cold worked alloy to not higher than 50° F. below the solvus and in the range 750° F. to 1,050° F. for 1 hour to 24 hours, advantageously at least 24 hours in order to ensure full recrystallization.

The invention provides products, which can be produced by the use of the process of the invention, having high yield strengths of 60,000 pounds per square inch (p.s.i.) and higher in combination with very good toughness and ductility, e.g., tensile elongations of 15 percent or greater. Yield strengths referred to herein are by the 0.2 percent offset method unless otherwise noted. Advantageously, the product is made with about 20 percent to about 40 percent nickel, more advantageously, 24 percent to 38 percent nickel, in order to obtain very high yield strengths of 90,000 p.s.i. and higher, e.g., 100,000 or 105,000 p.s.i. with 25 percent nickel. In connection with obtaining very high yield strength along with good ductility and other characteristics, e.g., fatigue strength, it is to be understood that the balanced two-phase structure is especially advantageous for these objects. For most practical commercial production purposes and in order to achieve good control of the zinc content, the product is produced with about 8 percent to about 40 percent nickel. With less than 8 percent nickel, the tolerance for variation in zinc is very low, only about plus or minus 1.2 percent, and such close control may be very difficult in commercial production. With more than about 40 percent nickel in the alloy, control of the zinc content is difficult due to volatilization at the high melting points of such alloys and special techniques, e.g., powder metallurgy or pressure melting, may be necessary in order to prepare the alloy.

Within the range of 8 percent to 40 percent nickel and with zinc and copper in accordance with the solvus relationships and/or the shaded area on the drawing, the low nickel alloys containing 8 percent to about 20 percent nickel are characterized by good tensile and fatigue strengths, e.g., 65,000 to 90,000 p.s.i. yield strength, while also being soft and highly malleable at normal hot working temperatures, such as employed in brass mills, and not requiring a rapid quench after solution annealing. The medium nickel alloys containing at least about 20 percent, e.g., 21 percent to 33 percent nickel, are characterized by higher strengths, e.g., yield strengths of about 90,000 to 105,000 p.s.i. although being somewhat stiffer at hot working temperatures and requiring rapid cooling from the solution annealing temperature. Higher nickel alloys containing at least 33 percent, e.g., 34 percent, to 40 percent nickel, are advantageous from the viewpoint of corrosion resistance and have very good strengths of the order of 95,000 p.s.i. to 100,000 p.s.i. yield strength. Control of the composition of these high nickel alloys becomes more difficult as the nickel content approaches 40 percent.

Further advantageous embodiments and advantages will become apparent hereinafter, inter alia, from the following illustrative examples which are given for the purpose of giving those skilled in the art a better understanding and appreciation of the advantages of the invention.

A number of copper-nickel-zinc alloys, including the alloys referred to as alloy Nos. 1 through 7, having compositions in accordance with the invention were prepared by air melting electrolytic copper and electrolytic nickel together and adding zinc pellets, or a zinc-nickel master alloy in the higher nickel compositions, with the melt at a temperature a little above the liquidus. When all the zinc was added, the melt temperature was raised to the pouring temperature, about 150° F. above the liquidus, finished with 0.1 percent titanium addition and poured into ingot molds. Chemical compositions of alloys 1 to 7 are set forth in the following table 1. The ingots of the alloys were hot worked to reduce the cross section size and break up the as-cast structure; alloys 1, 2 and 4 being extruded to ¾-inch diameter rod; alloys 5, 6 and 7 being extruded to 1.5 -inch diameter rod; alloy 3 was forged and hot rolled to ½-inch plate. Generally, hot working temperatures were about 1,400° F. to 1,600° F. with the lower temperatures being used for the lower nickel contents in order to minimize grain growth. Prior to hot working the alloys were homogenized by soaking about 2 hours to 4 hours at 1,500° F. to 1,600° F.

Wrought and heat treated alpha-beta microstructured products in accordance with the invention were prepared from alloys Nos. 1 trough 7 by the following processes P–I and P–II in accordance with the invention as follows. In P–I, applied to alloys 1 through 4, the alloy was solution treated by heating at 1,150° F. for 1 hour and water quenching, then cold rolling to 85 percent reduction in area and thereafter heating the cold rolled alloy at 900° F. for 24 hours followed by air cooling. In process P–II, applied to alloys 5, 6 and 7 the alloy was solution treated by heating to 1,200° F. for 1 hour and water quenching, then cold rolling to 82 percent reduction in area and thereafter recrystallization-precipitation treating by heating at 1,020 F. for 4 hours followed by air cooling. The resulting products were in the form of 0.080-inch thick rolled strip. Mechanical characteristics of the products produced by processes P–I and P–II were confirmed by tests of standard strip tensile specimens with a 1-inch by ½-inch gauge section and the thus-obtained room temperature tensile test results are set forth in the following table I.

TABLE I

	Composition				Product characteristics		
	Ni, percent	Cu, percent	Zn, percent	Process	0.2% Y, k.s.i.[1]	UTS, k.s.i.[2]	Elong., percent[3]
Alloy:							
1	10.0	51.7	[4]38.3	P–I	67.7	89.6	32
2	14.7	49.2	[4]36.1	P–I	69.4	94.2	29
3	15.4	48.3	[4]36.3	P–I	81.5	99.9	24
4	19.2	45.8	[4]35.0	P–I	90.1	101.3	21
5	25.5	Balance[5]	34.4	P–II	105.5	118.9	17
6	30.2	do	33.1	P–II	98.1	121.1	26
7	38.1	do	31.7	P–II	98.2	129.4	28

[1] Yield strength at 0.2% offset in 1,000 p.s.i. units.
[2] Ultimate tensile strength in 1,000 p.s.i. units.
[3] Tensile elongation in percent.
[4] Balance.
[5] By difference.
[6] 0.8% Mn and 0.1% Ti added to melt.

It is to be understood that the strengths of the two-phase products of the invention are much greater than the strengths obtained with alloys of corresponding compositions in the solid solution condition. For instance, alloys 1 and 7 when in the solid solution condition had 0.2 percent yield strengths of 26,400 p.s.i. and 52,000 p.s.i. ultimate tensile strengths of

64,000 p.s.i. and 108,400 p.s.i. and elongations of 65 percent and 24 percent, respectively. It is notable that with compositions having nickel contents of about 30 percent and 37 percent, the ductility of the high strength two-phase products of the invention, as evidenced by tensile elongations, was as good as or better than the ductility of the solution-treated alloys of the corresponding compositions.

Fatigue testing confirmed that the alloy has high fatigue strength that is substantially enhanced over the fatigue strength of conventional copper-nickel-zinc products such as nickel silvers. A fatigue specimen machined from the strip product of alloy 3 produced by process P–I successfully survived, or "ran out", without fracture when subjected to cyclically applied reversed bending stresses of 40,000 p.s.i.

Of further advantage, the product of the invention has been found to exhibit desirable high ratios of the 0.01 percent and the 0.02 percent offset yield strengths to the 0.2 percent offset yield strength, for example, 0.01 percent yield:0.2 percent yield ratios of 0.68:1 and 0.87:1, and 0.02 percent yield:0.2 percent yield ratios of 0.85:1 and 0.96:1, were obtained with alloys 6 and 7, respectively. These results are illustrative of high elastic limit characteristics that are beneficial for springs and other articles subjected to high elastic strain in use.

The wrought and heat treated two-phase product can be cold worked, if desired, to reduce the cross section or change the shape of the product or to further harden the product. A highly useful feature of the two-phase product is that the product can be heavily cold worked and then given a second recrystallization-precipitation heat treatment without causing any serious degradation of tensile characteristics The following table II shows tensile characteristics and hardness test results obtained with strip products made by processing alloy 3 in accordance with the process of the invention, both without he additional cold work, and in the fourth instance with a second heat treatment, after the first recrystallization-precipitation heat treatment.

TABLE II

Process	0.2% Y k.s.i.[1]	UTS k.s.i.[2]	Elong. percent[3]	Hard. R30T[4]
ST plus 80% CR plus RPHT	81.1	107.9	18	79
ST plus 80% CR plus RPHT plus 20% CR	116.1	131.1	5	84
ST plus 80% CR plus RPHT plus 50% CR	119.9	145.2	3	85
ST plus 50% CR plus RPHT plus 70% CR plus RPHT	79.6	99.8	24	79

[1] Solution treatment at 1,150° F. for 1 hour and air cool.
[2] Percent reduction by cold rolling.
[3] Recrystallization-precipitation heat treatment at 900° F. for 24 hours and air cool.
[4] Rockwell superficial hardness, 30T scale.

The two-phase product has also been produced in form of wire by cold-drawing the alloy in the solution-treated condition and then recrystallization-precipitation (RP) heat treating the wire; also, the RP heat treated wire has been again drawn and again RP heat treated with good results, thus confirming the utility of the process for multiple-pass drawing of wire.

The electrical conductivity of the product is of the general order of that of commercial nickel silvers of similar nickel levels. Examples of products of the invention containing 10 percent, 15 percent and 20 percent nickel had electrical conductivities of 7.9 percent, 6.8 percent and 5.9 percent IACS (International Annealed Copper Standard). It will apparent understood that the conductivity will generally decrease with increasing nickel. microstructures 800° F.

It is understood that temperatures and times required for recrystallization are codependent with alloy composition and degree of cold work. Accordingly, it is understood that the process of the invention is controlled, within the ranges set forth herein, with regard to alloy composition, degree of cold work and heat treating time and temperature to result in simultaneous recrystallization and precipitation. The techniques for the required control are apparent from the foregoing examples and other disclosures. As an additional guide to facilitate controlling the process, the following results of microstructures obtained with various processing of alloys 1, 2 and 3 are set forth in table III which illustrates many satisfactory procedures which provided satisfactory microstructures A, B, C and D, and also illustrates other procedures resulting in unsatisfactory microstructures E, F and G, which are to be avoided. In this connection, it is noted that particularly consistently good results were obtained when alloys 1, 2 and 3, containing 10 percent to 20 percent nickel, were cold

TABLE III.—MICROSTRUCTURES

Heat treatment in cold worked condition

		Temperature								
		700° F.			800° F.			900° F.		
	Percent cold worked	Hours								
		2	6	24	2	6	24	2	6	24
Alloy:										
1	72	G	G	G	G	C	C	C	A	A
1	85	A	A	A	A	A	A	A	A	A
1	96	A	A	A	A	A	A	A	A	A
2	72	—	—	—	—	F	D	E	—	B
2	85	F	G	E	E	A	A	E	B	A
2	96	F	G	A	A	A	A	A	A	A
3	72	—	—	—	—	—	E	E	—	D
3	85	F	F	G	F	E	A	D	B	A
3	96	F	G	E	E	A	A	A	A	A

Note: Percent work=Percent reduction in cross-sectional area by cold working.
A=Very good—Balanced two-phase microstructure; alpha fully recrystallized; coring minimal or nonexistent; beta finely divided equiaxed and uniformly intergranularly distributed throughout alpha matrix.
B=Satisfactory—Two-phase microstructure; alpha fully recrystallized; minor coring apparent by moderate beta concentration.
C=Marginally satisfactory—Two-phase microstructure; about 80% alpha recrystallized; some beta not equiaxed.
D=Marginally satisfactory—alpha fully recrystallized but beta not completely equiaxed.
E=Not satisfactory—alpha fully recrystallized; substantial beta-free cored areas.
F=Not satisfactory—alpha not recrystallized; beta on slip lines and on grain boundaries.
G=Not satisfactory—alpha not recrystallized; heavy beta concentration on slip lines and on grain boundaries.
—=Not examined.

worked at least 85 percent and heat treated at 800° F. to 900° F. for 24 hours; longer heat treatments, e.g., 100 hours or more, would not be detrimental. It should be further noted that as the nickel is increased, it is beneficial to increase the degree of cold working, the heat treat temperature and/or the heat treat time.

The fine alpha-beta structured product of the invention provides extraordinarily high formabiltiy at elevated temperature. For example, an ingot of alloy 3 was hot rolled from 4-inch thickness to ½-inch plate at 1,500° F. The hot rolled plate was solution annealed at 1,250° F. for one-half hour, air cooled, then cold rolled at room temperature to 0.10-inch thick strip (80 percent cold work) and thereafter recrystallization-precipitation heat treated to 950° F. for 4 hours and air cooled. The product produced by this process of the invention had a balanced two-phase microstructure typical of the microstructure illustrated in FIG. 2 of the drawing. Tensile specimens with a 2-inch by ½-inch gauge portion (0.10-inch thick) were machined from the recrystallization-precipitation treated strip. Straining such a tensile specimen of the thus produced product of alloy 3 in tension at a constant elongation rate starting from an initial strain rate of 0.025-inch per inch per minute at 900° F. resulted in neck-free elongation of 305 percent and thus demonstrated that the product had very high formability of a superplastic nature. Moreover, metallurgical inspection of the product after being elongated over 300 percent showed that no grain growth occurred during the elongation. Another tensile specimen of the fine alpha-beta alloy 3 product was likewise, stretched at 900° F., except that the elongation rate was gradually increased from 0.002 to 0.05 inch per minute and resulted in a neck-free elongation of about 300 percent without fracture. The unusually high formability of the product at elevated temperatures, such as tensile elongation of 200 percent or greater at temperatures of about 750° F. to about 1,000° F., provides special utility for hot-forming the product into articles having special shapes of highly elongated or deep-drawn, or other greatly stretched, configurations by forming methods such as press forging drawing, blow or vacuum forming and others. Furthermore, the hot formability characteristics of the product enable hot-working the product at desirable low working loads, e.g., low tensile-stretching loads or low roll-separation forces.

The product has generally good corrosion resistance providing utility in fresh water, salt water and other environments. However, the good corrosion resistance of the product does not generally extend to cover resistance to stress-corrosion cracking in ammonia and if the product is to be used under stress while in contact with ammonia, the product should contain at least about 33 percent nickel and advantageously, for protection against stress-corrosion cracking, should contain 37 percent or more nickel.

The present invention is applicable in the production of strong and ductile corrosion-resistant wrought products including sheet, strip, plate, bar, wire and rolled or extruded shapes, e.g., channels, T-sections, etc. Moreover, the invention is particularly applicable in the production of usefully and/or ornamentally shaped articles, including tableware, e.g., forks, spoons, butter knives, gravy boats, cream pitchers, and other items commonly referred to as holloware, and including springs, e.g., barometer springs, diaphragm springs and electrical contactor springs, musical instrument keys, surgical and medical instruments, and also costume jewelry. Furthermore, the product is also desirable for use as the underbody of an article cladded with another metal, especially as an underbody for cladding with silver as certain of the compositions have a color close to that of silver.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A wrought metal product having a microstructure consisting essentially of a fine-grained alpha phase matrix and fine beta phase particles dispersed discontinuously and intergranularly in the alpha phase matrix and composed of an alloy composition selected from the group of alloys in the copper-nickel-zinc alloy system characterized by an alpha/alpha-plus-beta solvus temperature of about 800° F. to about 1,200° F.

2. A product as set forth in claim 1 characterized by a room temperature yield strength of at least about 60,000 pounds per square inch.

3. A product as set forth in claim 1 wherein the average alpha grain size and the average beta particle size are not greater than about 10 microns.

4. A product as set forth in claim 1 composed of an alloy composition represented by a point in the area bounded by the line ABCDEFGA on FIG. 1 of the accompanying drawing.

5. A product as set forth in claim 1 composed of an alloy composition represented by a point within the area bounded by the line BCFGB on FIG. 1 of the accompanying drawing.

6. A product as set forth in claim 1 comprising at least about 33 percent nickel.

7. A product as set forth in claim 1 characterized by a tensile elongation of at least about 200 percent at a temperature in the range of about 750° F. to about 1,000° F.

8. A product as set forth in claim 1 comprising 8 percent to 40 percent nickel, zinc in an amount not less than the percentage determined by the relationship

$$\%Zn=38-0.23(\%Ni)$$

and not greater than the percentage determined by the relationship

$$\%Zn=42-0.23(\%Ni)$$

and balance essentially copper.

9. A product as set forth in claim 1 containing lead in an amount up to about 2 percent.

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