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COPPER-NICKEL-TITANIUM ALLOYS

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This invention relates to improved copper-nickel-titanium alloys of the solid solution type.

Hitherto it has been proposed to utilize the metal titanium as a deoxidizing agent for alloy steels and the like in which the residual content of titanium contemplated was very small, usually less than .1 percent. It has been further proposed to use titanium as a toughening agent or grain refiner in which cases the alloy may have some 1 percent of titanium retained, although several disclosures specify ranges of titanium for such purposes up to 10 percent. It is an object of the present invention to provide improved hardenable nickel alloys by combining with a suitable alloy, referred to as the base alloy, quantities of titanium and titanium-like elements.

It is a further object of this invention to confer hardening properties upon particular base alloy compositions chosen to provide other desirable properties, whereby not only the hardness but the elastic strength and breaking strength of the base alloy is increased without materially changing its other characteristic properties.

It is a still further object of this invention to alloy a suitable hardening agent with a nickel-bearing base material and subject the resulting alloy to a particular heat treatment to develop and control increased strength properties. These and other desirable advantages of the present invention will be set forth and described in the accompanying specification, certain preferred compositions being given by way of example only, for, since the underlying principles may be applied to other specific compositions, it is not intended to be limited to those herein shown except as such limitations are clearly imposed by the appended claims.

The present invention comprehends a wide variety of base alloy compositions and three preferred hardening agents, as will be described more in detail hereinafter. The preferred base alloy which is particularly amenable to the proposed treatment may be defined as nickel-bearing solid solutions having the face-centered cubic lattice type of crystalline structure. The claim for this broad definition is predicated on experimental work with six distinct alloy series of this type in addition to the metal nickel, all of which behave substantially similarly, and which behavior will be described more in detail below. No exceptions to this definition have yet been encountered, although the degree of hardening displayed by different combinations of base alloy and hardening agent, of course, vary somewhat in degree. In one such series, viz., iron-nickel-chromium-titanium, the hardening characteristics were displayed in alloys having ranges of nickel content varying from substantially 6 to 96 percent.

The preferred hardening agents comprehended within the spirit and scope of this invention are titanium, aluminum, and zirconium, and it is apparent that the hardening characteristics herein disclosed may be properties or functions of the boron and the titanium groups of the periodic classification of the elements according to Mendeleeff. Of these hardening agents titanium has been found to be the more useful from the standpoint of developing physical properties of engineering value combined with practical working qualities.

For the purposes of illustration, in order to more clearly set forth the novel features of the present invention, the characteristics of iron-nickel base alloys alloyed with titanium as a hardening agent will be discussed. Nickel-iron alloys which include from about 25 percent to substantially 100 percent nickel in their composition are soft and relatively unaffected in hardness by heat treatment. Titanium is soluble in these alloys and, if completely dissolved therein, the resulting ternary alloys retain substantially the original soft character. If a sufficient amount of titanium be added, however, the resulting alloys are soft only when cooled rather rapidly from a high temperature; if reheated to some lower temperature range, or allowed to cool rather slowly through this range, a substantial rise in hardness occurs. A still further increase in titanium content causes the alloys to become increasingly hard, even when subjected to rapid cooling from high temperatures, yet these alloys change somewhat in hardness with heat treatment. These characteristics in a series of iron-nickel alloys containing 35 percent nickel and varying amounts of titanium are shown in the following table:

Number	1	2	3	4	5	6	7
Percent titanium	0	.49	1.31	2.20	3.13	4.00	6.71
Brinell (1000° C. air cool)	132	131	137	151	178	268	393
(700° C. 3 hrs. water quenched)	132	138	197	307	327	371	380

The desirable range of titanium to be added to this particular base is from substantially 1 percent, at which point hardening begins, to about 4 percent, at which point the malleability of the alloys becomes impaired. The hardened alloys in common with iron-nickel alloys generally are characterized by their toughness, resistance to attack by non-oxidizing acids, ferro-magnetism and high electrical resistivity. With an increase in the nickel content of the base alloy, the desirable range of titanium, as just defined, remains substantially the same up to 75 percent nickel content, but the capacity for hardening displayed by the alloys under consideration, steadily diminishes with increase in nickel content up to 99% with a range of about 150 to 225 Brinell hardness units. Within the range of 75 to 96 percent nickel content, the minimum titanium content necessary to develop hardening, increases from about 1 percent to somewhat more than 4 percent, the amount being roughly proportional to the excess of nickel over 75 percent. Within this range the hardness differential developed by heat treatment is from about 75 to substantially 100 Brinell units.

Titanium when added to many other nickel alloys of the face centered cubic lattice type previously noted, permits the formation of alloys having hardening characteristics similar to the iron-nickel-titanium alloys described. Among these other base alloys may be mentioned: Iron-nickel-copper; iron-nickel-chromium; iron-nickel manganese; nickel-copper; nickel-chromium, and nickel metal. The following table shows several malleable alloys exemplifying this fact, the hardness numbers being expressed in Brinell units:

Number	8	9	10	11	12	13	14	15	16	17	18	19	20
Ni	63.4	43	30	35	23.3	18.4	15.3	35.5	93	80	20	20	74
Fe	3.1	35	58	61	65	66	66	57	1.2	9	12	3	12
Cu	27.2	19	8.0	1.1							64	76	10
Cr					7.9	11.8	14.5			8.0			
Mn								5.1					
Ti	1.9	3.0	2.3	2.3	2.5	2.6	2.5	1.6	3.0	3.0	4	1	4
Soft (1000° C. water quench)	130	127	157	159	154	153	152	126	194	165	300	164	178
Hard (tempered 600–700° C.)	237	271	302	315	315	304	284	266	284	317	321	200	235

The ranges of the several elements in addition to titanium, may be extended as follows: copper .5–90%, chromium 3–30%, nickel 2–99%, and iron 2–90%, the titanium being replaceable, under the conditions discussed more in detail hereinafter, by from .5–10% of titanium-like metals such as aluminum and/or zirconium. These elements may be associated with each other in any desired amounts to give compositions having certain specified characteristics.

The preferred range of titanium is substantially from 1 to 4 percent. This range is determined approximately by the first appearance of hardening and the substantial disappearance of hot malleability. When it is desired to retain good hot and cold working properties in order to permit shaping by forging, hot rolling, cold rolling, drawing, or plastic deformation generally, full advantage cannot be taken of the maximum titanium content. In such cases it is preferable to employ titanium contents ranging from 2.2 to 3.2 percent for alloys having a low carbon content and in which the base is nickel-iron, nickel-copper-iron, and nickel-chromium-iron. It will, of course, be understood that in case of castings where workability is not a factor to be considered, a much greater range of titanium is permitted with a correspondingly greater degree of hardness. In such cases as much as 10 percent titanium may be used to advantage.

As has been intimated hereinbefore, desirable results may be obtained by substituting aluminum and/or zirconium for the titanium. In the following table a few typical alloys are given by way of example.

	Number	21	22	23	24
	Fe	55	56	68	62
	Ni	38.7	33.6	17.4	34.6
	Cu		5.9		
	Cr			8.2	
	Al	5.1	4.4	5.4	
	Zr				2.6
Brinell hardness Number	Soft (1000° C. w. q.)	154	155	172	157
	Hard (600°C. temp.)	218	256	282	183

In the case of aluminum, the content of this element necessary to develop suitable hardening response varies from about 2.5 to substantially 6 percent, the latter percentage marking the approximate upper limit of forgeability. A preferred range is from 5.0 to 5.5 percent.

When titanium is used as an alloying element, the use of commercial ferro-titanium may introduce appreciable quantities of aluminum and silicon into the metal, both of which elements will appear in the resulting alloy. This content of aluminum is not harmful and it has now been found in fact that the use of even higher contents of aluminum in combination with titanium as hardening agents offers certain advantages, notably in accelerating the rate at which the hardening reaction occurs. As an example of this discovery, the nickel-iron-titanium alloy including 34.8 percent nickel, 2.2 percent titanium, and 0.3 percent aluminum, showed no appreciable hardening when air-cooled from 1000 degrees centigrade. A similar alloy including 34 percent nickel, 2.5 percent titanium, and 1.9 percent aluminum increased in hardness about 110 Brinell units on air-cooling. Both alloys hardened to about 320 Brinell units when furnace cooled. It will also be appreciated that by the use of hardening agents in multiple as herein described, it is possible to secure marked economies in manufacture due to the ability to use cheaper addition materials without in any way sacrificing the good results desired in the finished product.

The diversity of base compositions amenable to hardening by titanium and aluminum has been described. No common alloying elements in amounts less than 2 percent have been found to interfere with this hardening characteristic with the exception of aluminum and carbon. The effect of aluminum when combined with titanium has just been described. Since carbon forms an inert titanium carbide, its presence with titanium is highly detrimental. This is due to the fact that although the total titanium content may be great enough to indicate vigorous hardening, the alloy is, in fact, devoid of hardening response. It is highly desirable, therefore, to keep the carbon content as low as is metallurgically feasible. Alloys of this type have been produced with as little as .01 percent carbon, yet melts containing as much as 0.40 percent carbon have been produced which displayed good hardening properties, although an inefficiently high titanium content in the alloy was necessary.

It is considered to be within the scope of this invention to provide, in addition to the major elements of composition, such other elements as are commonly used in metallurgy to aid in refining, purifying, degasifying, and otherwise treating the alloy to insure its production in sound, tough, malleable form. These auxiliary elements are:

	Percent
Manganese	up to 5
Silicon	up to 5
Aluminum	up to 1
Vanadium	up to 1
Zirconium	up to 1
Titanium	up to ½
Calcium	up to ½
Magnesium	up to ½
Boron	up to ½

The nature and quantity of these accessory elements is determined by the nature of the base alloy in question.

Many characteristics of the hardening action developed by titanium and its equivalents, as described hereinbefore suggest that it is of the so-called "precipitation" type, and that nickel, in association with titanium and/or aluminum, is withdrawn from solid solution concurrently with the rise in hardness on heat treatment. Of course, this is only a possible theory and it is to be understood that we are not bound to this theory.

To bring the alloys under consideration into the softest working condition, the heat treament required in all cases is a not too slow cooling from above a minimum temperature. Most efficient results are obtained when this minimum temperature is exceeded, but the temperature margin by which it is exceeded is not of very great importance, the upper limit usually being that at which an undesirable coarsening in grain size occurs. The minimum softening temperature varies directly with increase in content of the hardening element or elements, and also varies to some extent with the composition of the base alloy. For contents of titanium and/or aluminum which yield malleable alloys, this minimum temperature is generally from 750 degrees centigrade to 850 deg. centigrade, and can easily be established for a particular alloy. As a general rule the entire group of alloys herein described respond well to a range of softening temperatures varying from 900 deg. C. to 1050 deg. C. The rate of cooling required to avoid hardening is not great, and air cooling will usually prove fast enough, although cooling in water or in oil is permissible.

Where it is desired to heat treat the alloys in order to harden them, the treatment is much more variable. Variations in composition of the base metal, and of the hardening elements affect both the temperature at which the desired hardening is most effectively produced, and also the rate at which it occurs. In all cases hardening occurs over a considerable range of temperatures, and the lower the temperature at which this can be carried out, the greater will be the hardness ultimately developed. Since the rate of hardening diminishes as the temperature is decreased, an optimum hardening temperature may be appropriately designated.

With a hardening treatment which includes holding the alloy at a fixed temperature for several hours, the preferred hardening temperature is substantially 700 deg. C. for alloys in which titanium is the hardening element, and about 600 deg. C. when aluminum or zirconium is the hardening element. It is to be noted that when chromium does not exceed about 5 percent, good hardening may be produced by furnace cooling from the softening range. When the chromium content exceeds this value, the hardening reaction proceeds sluggishly, and considerably more time is required in order to develop full hardness. High chromium alloys containing up to 30% chromium may show very little hardening on furnace cooling.

When it is desired to develop the maximum hardness of a given alloy, it has been found advantageous to carry out the hardening operations in several steps at progressively lower temperatures and preferably with the duration of heating increasing at the lower temperatures. The temperature range in which this incremental hardening may be carried out is from the minimum softening temperature above described, down to about 500 deg. C. As a particular example, an alloy of a composition including

Ni	22.0
Cr	6.7
Ti	2.6
Fe	Bal.

having an initial Brinell hardness of 148 hardened to 290 Brinell after twenty-four hours of treatment at 700 deg. C. When an incremental hardening heat treatment was given to this alloy, a hardness of 340 Brinell units was secured, the particular treatment included heating at 750° C. for two hours, followed by heat treatment at 600 deg. C. for five hours, and at 600 deg. C. for twenty-three hours.

On the other hand, for the purpose of improving toughness and ductility of the hardened alloy, the termination of the hardening operation may include the step of reheating to a temperature higher than the last preceding step, but still within the range of temperature in which the particular alloy is hardenable.

A further example may be given in which the hardening characteristics as described hereinabove are combined with martensitic hardening of the type commonly observed in air-hardening steels. This combination occurs in marginal austenitic nickel-content ferrous alloys of the nickel, nickel-chromium, nickel-copper, nickel-manganese and related series in which the iron content is up to about 10 percent lower than that at which martensite ceases to be a constituent under ordinary conditions of cooling.

Alloys of the aforesaid type when heat treated develop a strengthening precipitate, accompanied by a change in composition of the residual matrix sufficient to shift the latter within the range of compositions which have a true allotropic transformation, and hence, at suitable cooling velocities, can be transformed at least partially into martensite. The following are two examples of alloys in which the effect is characterized by intense hardening.

Ni	Cr	Ti	C	Al	Brinell hardness number	
					1000° C. w. q.	Tempered
15.7	10.3	2.7	.08	--------	143	420
20.9	8.2	2.7	.03	1.8	159	498

These alloys were both completely austenitic and non-magnetic when in the soft condition, but became magnetic and partially martensitic after heating between 600 and 700° C. followed by cooling in the air.

As exemplifying the physical properties produced in malleable alloys of the type under consideration, the following table is included:

No.	Ni	Cu	Cr	Ti	Fe	Temper	Prop. limit Psi	Ult. strength Psi	Elong. 2″ per-cent	Red area percent	Izod ft./lbs.
25	30.1	8.0	------	2.5	Bal.	Soft	24,800	87,600	37.5	65.1	----------
						Hard	110,000	192,000	16.0	33.0	----------
26	21.7	------	6.3	2.4	do	Soft	34,600	87,800	35.0	59.8	----------
						Hard	77,400	158,000	22.0	47.8	----------
27	15.5	------	12.4	2.7	do	Soft	24,000	88,000	48	68	102
						Hard	--------	--------	--------	--------	--------
						Hard (a)	66,000	130,000	36	62	74
						Hard (b)	80,000	160,000	22	18	50

(a)—700° C. temp.
(b)—Incremental temper.

In addition to exhibiting these high physical properties at room temperatures, the high strength and elastic properties shown may be retained at high temperatures, provided that the base alloy is of a suitable type; iron-nickel-chromium is appropriate, and the titanium alloy with this base shows excellent strength properties at temperatures up to the hardening temperature. The steel designated as number 27 in the above table shows the following characteristics when broken in tension at 600 deg. C. after previous full hardening:

90,000 psi PL.
125,000 psi Ult.

25% elong. in 2″
12% red. area

Such alloys are particularly suited for purposes involving considerable heat and load such as obtained in steam and internal combustion turbines, as well as in many chemical processes, a particular example being that of tube stills and like apparatus which may be used in oil-cracking and oil refining.

Many alloys, in particular steels, exist which have hardness and tensile properties equal to or even excelling the alloys of the present type. The advantage of the latter lies in the unique fact that the present hardening elements may add hardening properties to particular base alloys without detriment to their other distinctive properties, thus affording a combination of strength with other special qualities not previously possible. For example, the addition of titanium to austenitic nickel-chromium steels imparts hardness and high elastic properties without interfering with the valuable corrosion and heat resisting qualities of the latter. In particular cases in which a property is closely associated with a specific nickel content, e. g., low expansivity in nickel-iron alloys, a slight adjustment of composition may be necessary in the hardened alloy. This adjustment generally involves a small increase in nickel content.

It will now be appreciated that there has been provided an improved process for producing high strength alloys of the solid solution type containing nickel, which are initially soft and workable, which process comprehends the use of suitable amounts of hardening agents such as titanium, aluminum and/or zirconium. It is to be noted further that the hardenable alloys comprehended within the spirit and scope of the present invention, are adapted for a wide variety of uses, and more particularly for use in structures which can economically be made by plastic deformation such as drawing, pressing, etc., such formed articles being adapted to being suitably hardened by a heat treatment as set forth. Furthermore, the present invention has been described in conjunction with various compositions the nickel content of which may be applied to any of alloys disclosed herein. Thus, specific nickel alloys containing about 6% and about 15% referred to on pages 1 and 4, respectively, but these nickel contents or variations thereof within the scope of the present invention may be used in any of the present alloys. For example, a nickel alloy containing about 10% nickel, about 87% copper and about 3% titanium when in a soft condition resulting from quenching in water from 900° C. had a Brinell hardness number of 130 and when in a hard condition resulting from reheating to a temperature of about 600° C. to about 700° C. had a Brinell hardness number of 183.

This is a divisional application of Serial Number 566,311 filed October 1, 1931, Patent 2,048,166, and continuation in part application of our application, Serial No. 356,870, filed April 15, 1929, Patent 2,048,163.

What is claimed is:

1. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1 to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

2. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1 to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to

obtain a substantial increase in the hardness of the alloy.

3. A hard nickel-copper alloy containing about 2% to about 50% nickel, about 2.2% to about 3.2% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

4. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1% to about 10% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

5. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1% to about 4% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

6. A hard nickel-copper alloy containing about 2% to about 50% nickel, about 2.2% to about 3.2% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

7. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1% to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

8. A hard nickel-copper alloy containing about 2% to about 50% nickel, at least 1% to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

9. A hard nickel-copper alloy containing about 2% to about 50% nickel, about 2:2% to about 3.2% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

10. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1 to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

11. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1 to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

12. A hard nickel-copper alloy containing about 20% to about 50% nickel, about 2.2% to about 3.2% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

13. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1% to about 10% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

14. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1% to about 4% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

15. A hard nickel-copper alloy containing about 20% to about 50% nickel, about 2.2% to about 3.2% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

16. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1% to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

17. A hard nickel-copper alloy containing about 20% to about 50% nickel, at least 1% to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

18. A hard nickel-copper alloy containing about 20% to about 50% nickel, about 2.2% to about 3.2% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

19. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1 to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

20. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1% to about 10% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

21. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1% to about 10% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

22. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1 to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating the alloy to an elevated temperature below its melting point but sufficiently high to cause titanium to go into solution, quenching the alloy and reheating to a temperature below that of the initial heating but sufficiently high and for a period of time sufficient to obtain a substantial increase in the hardness of the alloy.

23. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1% to about 4% of titanium and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time and at a sufficiently high temperature between 750° C. and the melting point to dissolve at least a portion of the titanium in the alloy, cooling the alloy to a temperature below 750° C. and heating the alloy for a sufficient period of time and at a sufficiently high temperature below 750° C. to obtain a substantial increase in the hardness of the alloy.

24. A hard nickel-copper alloy containing about 10% to about 50% nickel, at least 1% to about 4% titanium, and copper constituting substantially the balance of the alloy, said alloy being age hardened by heating for a sufficient period of time at a sufficiently high temperature between 750° C. and the melting point of the alloy to cause at least a portion of the titanium to dissolve in the alloy, and cooling the alloy from the aforesaid temperature to about 500° C. at a rate sufficiently slow to cause a substantial increase in the hardness of the alloy.

25. A process for improving copper alloys including .1 to 4 per cent titanium which comprises quenching the said alloys at temperatures of about 650 to 1000° C. and then aging at about 250 to 600° C.

26. A process for improving copper-titanium alloys including a predominating amount of copper and some titanium which comprises cooling said alloys from temperatures of about 650° to 1000° C. and then aging them at about 250 to 600° C.

27. The process for treating an alloy consisting substantially of copper and titanium, the titanium being present in the alloy in but minor quantity, said process comprising heating said alloy to a temperature between about 650° C. to 1000° C., quickly cooling the alloy, and then reheating it to a temperature between about 250° C. to 600° C.

28. The process of treating an alloy consisting substantially of copper and titanium, the titanium being present in but minor quantities, said process comprising heating said alloy to a relatively high temperature, quenching the alloy, and then reheating it to a relatively low temperature to age-harden the alloy.

29. Heat-hardened copper-titanium alloys con-

taining titanium in quantities ranging from a small but detectable amount up to about 5 per cent by weight, the balance being substantially copper; said alloys having the tensile strength, electrical resistance and other properties produced by a heat treatment comprising heating said alloy to temperatures ranging from about 650° to 1000° C., followed by aging at temperatures of from about 250° to 600° C.

30. Heat-hardened copper-titanium alloys containing titanium in quantities ranging from a small but detectable amount up to about 4 per cent by weight and also containing up to 10 per cent of additional hardening metals selected from a group consisting of nickel, chromium, manganese, iron, cobalt and molybdenum; said alloys having the tensile strength, electrical resistance and other properties produced by a heat treatment comprising heating said alloy to temperatures ranging from about 650° to 1000° C., followed by aging at temperatures of from about 250° to 600° C.

31. The process of treating an alloy containing titanium in quantities ranging from a small but detectable amount up to about 4 per cent by weight and also containing up to 10 per cent of additional hardening metals selected from a group consisting of nickel, chromium, manganese, iron, cobalt and molybdenum, said process comprising heating said alloy to temperatures ranging from about 650° to 1000° C., followed by aging at temperatures of from about 250° to 600° C.

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