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AGE HARDENABLE, NICKEL-IRON-CHROMIUM-TITANIUM ALLOY POSSESSING CONTROLLED THERMOELASTIC PROPERTIES

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Fig. 1.

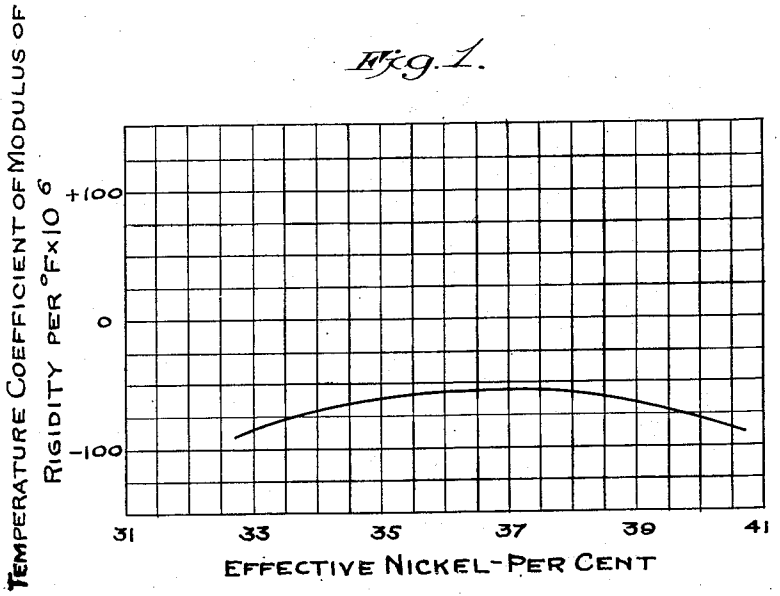
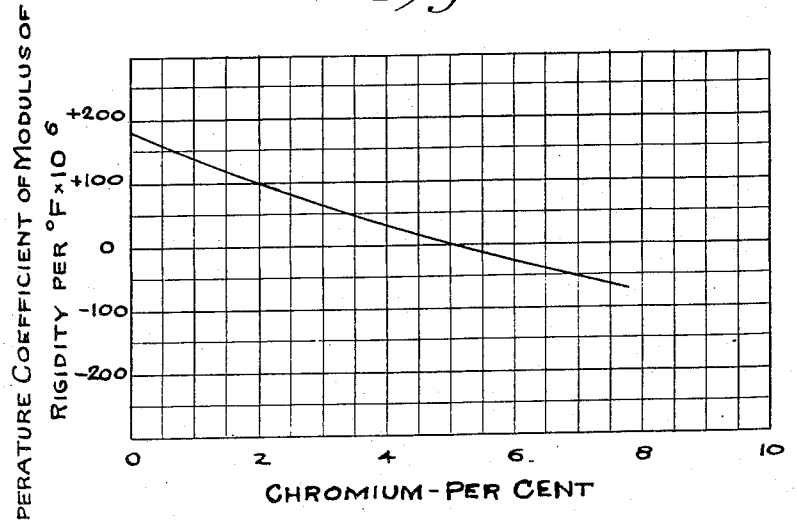


Fig. 2.



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AGE HARDENABLE, NICKEL - IRON - CHROMIUM - TITANIUM ALLOY POSSESSING CONTROLLED THERMOELASTIC PROPERTIES

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5 Claims. (Cl. 148—31)

The present invention relates to improved age-hardenable controlled modulus alloys and to age hardened articles of manufacture made therefrom, and more particularly, to age hardenable controlled modulus iron-nickel-chromium alloys and articles of manufacture made therefrom for use in precision devices of resilient nature.

It is well known that the accuracy of precision devices of resilient nature, for example, chronometers, weighing scales, etc., are affected by changes in temperature. It has been suggested that these defects could be overcome by using materials made of alloys of substantially constant or controlled elastic modulus containing about 30% to 38% nickel, up to 12% chromium, and the balance iron. It is also known that part of the chromium may be replaced by one or more of the members of the group consisting of tungsten, molybdenum, vanadium, aluminum and silicon in amounts ranging from traces, e. g. .001% up to 4% or even more. These metals, like chromium, lower the temperature coefficient of the modulus of elasticity of iron-nickel alloys containing about 35% nickel so that the coefficient has a value of zero or is slightly negative or positive as desired, when measured at usual temperatures. Tungsten, molybdenum and vanadium also served to increase the base hardness of the alloys. These alloys are frequently referred to as controlled or constant modulus alloys. By "constant modulus," we mean that the temperature coefficient of the modulus of elasticity is substantially zero. Alloys referred to as "controlled modulus" alloys will have a small positive or negative value for the temperature coefficient of modulus of elasticity as is required to give the best overall result and will include those showing a zero change in modulus with temperature. Generally speaking, these modulus changes refer to changes observed at temperatures ranging from ordinary atmospheric temperatures up to about 200° F. Since these alloys are austenitic, they can be hardened only by cold work and as a consequence, many potential applications have been hindered by the fact that the alloys did not possess the high strength and other mechanical properties required in these applications. Attempts to obtain the desired mechanical properties by cold working about 75% to 90% did not produce completely satisfactory material when carried out into industrial scale operation. Serious difficulties were also constantly encountered in cold working the alloys to the required heavy cold reductions. Even excessive amounts of cold work yield only moderately good mechanical properties and entail serious difficulties in production and subsequent fabrication.

Although many attempts were made to remedy the aforementioned shortcomings, none as far as we are aware, was entirely successful, produced satisfactory results and could be carried into practical and economic industrial scale operation.

We have discovered certain iron-nickel-chromium-titanium alloys which can be age hardened and in which the nickel, chromium and titanium are critically related to yield controlled or substantially constant thermo-elastic properties akin to those exhibited by the alloys of the Elinvar-type but exhibiting markedly superior mechanical properties, particularly high proportional limits. Titanium is added in critical and controlled amounts and a compensating adjustment is made in the nickel and chromium contents in special proportions to balance said nickel and chromium against titanium and any carbon which is present. The age hardening characteristics facilitate manufacture and avoid the necessity of the excessive cold working required with pre-existing materials.

It is an object of the present invention to provide improved age hardenable and age hardened controlled modulus iron-nickel-chromium-titanium alloys which contain controlled and adjusted proportions of nickel, chromium and titanium and in which the nickel and chromium are balanced against the titanium and any carbon present in the alloy.

It is another object of the present invention to provide improved age hardenable and age hardened iron-nickel-chromium alloys of the Elinvar-type containing controlled and balanced amounts of nickel, chromium and titanium and characterized by improved mechanical properties, including high proportional limits and tensile strength while achieving a substantially constant or controlled temperature coefficient of modulus of elasticity.

It is a further object of the present invention to provide, as articles of manufacture precision devices including resilient elements made of special age hardened ferrous austenitic alloys containing controlled and specially balanced amounts of nickel, chromium and titanium.

The invention contemplates a method of producing age-hardenable and age-hardened controlled modulus iron-nickel-chromium alloys and containing controlled amounts of titanium

and articles of manufacture for use in precision devices of resilient nature made therefrom, and possessing substantially constant thermo-elastic modulus combined with high mechanical properties in the age hardened condition, said process involving an adjustment, in special proportions of the nickel content and the chromium content to compensate for the alteration in thermo-elastic properties caused by the presence of titanium.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description taken in conjunction with the accompanying drawing in which:

Fig. 1 is a graph illustrating the effect of varying the effective nickel content upon alloys containing sufficient chromium to exhibit negative coefficients; and

Fig. 2 is a graph depicting the effect of varying the chromium content upon another series of alloys made in accordance with the present invention.

Broadly stated, the invention provides iron-nickel-chromium alloys of the Elinvar-type which contain controlled and critical amounts of titanium and which after age hardening heat treatment possess markedly increased mechanical properties combined with controlled or substantially constant thermo-elastic properties, e. g., a zero thermo-elastic coefficient. A strictly constant modulus alloy is not always desirable, since in practical applications, dimensional changes in the structure may require a slightly negative or positive thermo-elastic coefficient, in order to secure a minimum temperature coefficient for the whole device. The present invention provides alloys with constant or controlled coefficients of modulus of elasticity over a wider range of temperatures than is ordinarily obtained and, in addition, higher mechanical properties are obtained with greater ease of production and subsequent manufacture. Mechanical properties, especially proportional limit which is generally of controlling importance in resilient elements, in excess of those obtainable by cold working the ordinary alloys are produced in the alloys provided by the present invention.

The compositions that have been found to develop the above-mentioned desirable characteristics and properties are essentially alloys of iron, nickel and chromium to which about 1% to about 4% of titanium has been added. It has been found that when titanium is added to the Elinvar-type alloys, the thermo-elastic properties are adversely affected and are not as expected or desired. We have discovered that the composition of the titanium-containing alloys must be selected in accordance with certain special relationships between the alloying elements and that the various elements must be balanced against each other in special proportions to control the temperature coefficient of the modulus of elasticity. It has been found that the thermo-elastic properties are not solely dependent upon the total nickel for a fixed chromium content of the alloys, as in the case of ordinary alloys of the Elinvar-type, but are dependent upon the portion of the nickel content which has been termed herein the "effective nickel" content. Likewise, the thermo-elastic properties for a fixed nickel content are not solely dependent upon the total percentage of chromium-like metal, i. e., chromium plus any vanadium, tungsten, molybdenum, aluminum or silicon present as a replacement for chromium, but upon a relationship of chromium-like metal to titanium. In addition to titanium, the alloys may contain carbon, especially in industrial practice. While not a necessary element, commercial production methods often result in the introduction of some carbon, e. g., along with the titanium addition alloy. Carbon may be present in amounts up to about 0.2%, but it is preferred to maintain the carbon at low levels, e. g., up to .08%, in order that the maximum benefits of titanium be realized. The amounts of nickel and of chromium or chromium-like metals are dependent upon a relationship of carbon and titanium which has been termed herein the "non-carbidic" titanium. For practical purposes, the non-carbidic titanium is the total titanium content in weight percent less four times the carbon content in weight percent. The effective nickel content of the alloys provided by the present invention should be maintained within the range of about 34.5% to about 37.5%, or 39%, and the titanium content within the range of about 1% to 4%. The total nickel content of the alloys may be expressed by the following formula:

$$\text{Total Ni} = \text{Effective Ni} + K\ (\text{Non-carbidic Ti})$$

where K has a value of about 2.4. The total chromium percentage is expressed by the following formula:

$$\%\text{Total Cr} + \%\text{Non-carbidic Ti} = 4\% \text{ to } 9\%$$

The alloys of the present invention have the approximate composition set forth in the following Table I.

Table I

Element	Percentage
Titanium	1 to 4.
Carbon	Up to 0.2.
Effective nickel	34.5 to 37.5.
Total nickel	(34.5 to 37.5)+2.4 (Ti−4×C).
Chromium	(4 to 9)−(Ti−4×C).
Iron	Balance.

The total nickel content usually falls within the range of about 36% to about 47%. As pointed out hereinbefore, some carbon is usually present, e. g., 0.02% to 0.07%, and preferably less than about 0.08%. It is to be understood that carbon may be completely absent or may be present only in traces or small amounts of the order of 0.001%. In addition, the alloys may also contain small amounts of minor elements and impurities and when we say in the specification and claims that the "balance is iron," "balance is substantially all iron," etc., we include within the expression minor constituents and impurities, such as cobalt, manganese, zirconium, silicon, aluminum, sulfur, phosphorus and other elements commonly present in such materials in commercial practice. Thus, the alloys may contain from traces, say 0.001%, up to about 1% of silicon, up to about 1.5% manganese, up to about 1% aluminum, etc. Silicon and aluminum, as well as carbon, are often associated with the titanium used as an addition material. Manganese is often present for the purpose of improving the forgeability. As pointed out hereinbefore, the chromium may be replaced by other elements which have an effect similar to chromium, i. e., chromium-like metals, in amounts from traces, say 0.001%, up to about 4%, or even more, as is well known to those skilled in the art and when we refer to chromium in the claims we do not desire to exclude the presence of small amounts of chromium-like metals as

above indicated or as will have the same desired effect as chromium on the thermoelastic properties.

In carrying the invention into practice, it is preferred to maintain the titanium within the range of about 2% to about 3.25%, say about 2.7% titanium. The chromium content is preferably maintained within the range of about 6% to about 4.7%, say about 5%. Representative values of minor elements which may be present as a result of commercial practice include about 0.06% carbon, about 0.5% silicon, about 0.6% manganese, about 0.3% aluminum.

In order that those skilled in the art may have a better understanding of the present invention, illustrative examples of constant modulus alloys produced in accordance with the present invention are given in the following Table II.

Table II

Element	Alloy 1	Alloy 2	Alloy 3	Alloy 4
Nickel.....percent..	40	42	44	42
Chromium.....do....	6	5.4	4.7	5.2
Titanium.....do....	2	2.5	3.25	2.5
Carbon.....do....	0.06	0.06	0.06	0.06
Molybdenum.....do....				0.45

The influence of effective nickel content upon the temperature coefficient of one series of alloys is illustrated in Fig. 1. Fig. 2 shows the effect of chromium upon the temperature coefficient of the modulus of rigidity of an alloy containing 42% nickel, 2.6% titanium, 0.45% molybdenum, chromium in various amounts and the balance iron which has been subjected to an aging treatment at 1250° F. for 4 hours and furnace cooled. The values given herein for the temperature coefficient of the modulus of rigidity, i. e., the thermo-elastic coefficient, were determined by a torsion pendulum while the ambient temperature was changed through a series of values. The proportionate change in moduli with temperature in relation to the moduli at 0° F. determines the temperature coefficient.

For maximum mechanical properties, the alloys of the present invention are preferably subjected to a solution treatment prior to a moderate cold working operation and subsequently aged at temperatures between about 1100° F. and 1350° F. The usual solution treatment is accomplished by heating at about 1700° F. to about 1750° F. and rapidly cooling, e. g., oil quenching. Slow cooling from the aging temperatures is desirable from a standpoint of stability of properties.

Mere aging without cold working will increase the mechanical properties. Excellent high mechanical properties are obtained by cold working prior to the aging heat treatment and this treatment is ordinarily preferred. In some instances it may be convenient, particularly with alloys containing about 1.5% to 2% titanium, to cold work after aging heat treatment. Material cold worked with or without prior aging, requires a stress relief treatment to obtain stable thermo-elastic properties. Amounts of cold work up to about 35% or about 50% reduction in cross section which are readily attainable, appear very suitable to produce excellent high mechanical properties; whereas excessive amounts of cold work (75 to 99%) are necessary to produce high mechanical properties in Elinvar-type alloys.

For ordinary purposes a titanium content of about 2.4% to about 2.8% is satisfactory for high mechanical properties as shown in Table III. Somewhat higher mechanical properties may be obtained by increasing the titanium to higher levels, for example, about 3.5% titanium. The effect is reversed with lower titanium contents.

Table III

Alloy	P. L.	Y. S.	T. S.	T. E. C.	M. R.
Ordinary titanium-free.....	84,000	111,000	126,000	-5×10^{-6}	9.4×10^{6}
Aged titanium-containing.....	123,000	150,000	169,000	0	10×10^{6}

P. L.=proportional limit in pounds per square inch.
Y. S.=yield strength in pounds per square inch.
T. S.=tensile strength in pounds per square inch.
T. E. C.=thermo-elastic coefficient per °F.
M. R.=modulus of rigidity in pounds per square inch.

The ordinary constant modulus alloy, after water quenching from about 1750° F., was cold drawn 75% and treated for two hours at about 650° F. The age hardened alloy (alloy 5) contained 42.4% nickel, 5% chromium, 2.4% titanium and balance iron including 0.06% carbon, 0.56% manganese, 0.56% silicon and impurities, and was water quenched from 1750° F., subsequently cold drawn 35%, heat treated two hours at 1150° F. and furnace cooled.

High mechanical properties are obtained by aging at temperatures between about 1100° and about 1350° F. However, by varying the treatment within this range it is possible to vary the temperature coefficient of elasticity as desired within certain ranges. For a given alloy, the higher the aging temperature, the higher the temperature coefficient of elasticity. Similarly, the longer the period of aging at a given temperature, the higher the temperature coefficient of elasticity. Also, it appears that the more the cold work, the lower the temperature coefficient of elasticity. Slow cooling from the aging temperature usually results in appreciably higher proportional limits and more stable elastic properties. Table V shows the effect of varying the treatment upon the properties of alloy 5. The material in each instance was water quenched from 1750° F. prior to receiving the various treatments shown in Table IV.

Table IV

Treatment	Cold Work	Aging temp.	Aging time	Cooling rate
	Percent	° *F.*	*Hours*	
A	35	1,250	4	Furnace cooled.
B	35	1,150	4	Do.
C	35	1,150	2	Do.
D	50	1,150	2	Do.

Table V

Treatment	P. L.*	Y. S.	T. S.	T. E. C.	M. R.
A	117,000	142,000	169,000	$+15\times10^{-6}$	10.1×10^{6}
B	130,000	158,000	172,000	$+10\times10^{-6}$	10.0×10^{6}
C	123,000	150,000	169,000	0	10.0×10^{6}
D	117,000	149,000	174,000	-5×10^{-6}	9.9×10^{6}

*See Table III for key to symbols.

The present invention provides a method of producing improved age hardenable iron-nickel-chromium-titanium alloys, and articles of manufacture made therefrom, possessing predetermined high mechanical properties and predetermined controlled modulus and containing as essential ingredients about 1% to about 4% titanium, about 36% to about 47% nickel, a small but effective amount up to about 9% chromium, and

the balance substantially iron, in which carbon may be present up to about 0.2%, which comprises incorporating in an iron-nickel-chromium alloy a selected titanium content within said range corresponding to the predetermined desired mechanical properties, for example, proportional limit, and being larger the higher said desired properties, the nickel content of said alloy being proportioned within said range in accordance with the following formula:

$$\text{Total Ni} = \text{Effective Ni} + K\,(\text{Ti} - 4\times\text{C})$$

where the effective nickel is selected within the range of about 34.5% to about 37.5%, K being a constant with a value of about 2.4, and Ni, Ti and C being respectively the weight percent of nickel, titanium and carbon; the chromium content of said alloy being proportioned within said range in accordance with the following formula:

$$\text{Total Cr} = (4 \text{ to } 9) - (\text{Ti} - 4\times\text{C})$$

where Cr is the weight percent of chromium, whereby an improved age hardenable alloy is obtained combining high mechanical properties, for example, proportional limit, with controlled thermo-elastic properties, for example, temperature coefficient of modulus of elasticity, in the age hardened condition. Preferably the alloy is subjected to moderate cold working prior to an age hardening treatment in accordance with the procedure set forth hereinbefore.

The present invention provides as an article of manufacture, a precision device or instrument of resilient nature containing a resilient element or member made of the improved age hardened alloys provided by the present invention. Typical examples of such devices and elements or members include springs, for example, hair springs for watches and other chronometers, springs for weighing scales; tuning forks; Bourdon tubes; proving rings for testing machines, torsion and tension dynamometers, etc.

We are aware of the invention described in U. S. patents to Pilling and Merica, including U. S. Patent No. 2,048,167, and we do not claim any of the subject matter disclosed therein. The present invention is an improvement in the art of controlled and constant modulus iron-nickel-chromium alloys.

Although the present invention has been described in conjunction with preferred embodiments, it is 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.

We claim:

1. As an article of manufacture, an age hardened iron-nickel-chromium-titanium alloy possessing a temperature coefficient of modulus of elasticity having a small positive to negative value including zero and containing in weight percentage from 36% to 47% nickel; an effective amount up to 9% chromium; 1% to 4% titanium; up to 0.2 carbon; the percentage of nickel, titanium and carbon being such that

$$\text{Total Ni} - K(\text{Ti} - 4\times\text{C})$$

lies between 34.5% and 39%, and the percentage of chromium, titanium and carbon being such that

$$\text{Cr} + (\text{Ti} - 4\times\text{C})$$

lies between 4% and 9%, K being a constant having a value of about 2.4%, and Ni, Cr, Ti and C being respectively nickel, chromium, titanium and carbon in weight percentage; and the balance being substantially all iron whereby a novel age hardened iron-nickel-chromium-titanium alloy is obtained having a unique combination of properties including the aforesaid temperature coefficient of modulus of elasticity having a small positive to negative value including zero together with high mechanical properties.

2. As an article of manufacture, an age hardened iron-nickel-chromium-titanium alloy possessing a temperature coefficient of modulus of elasticity having a small positive to negative value including zero and containing in weight percentage from 38.5% to 45.3% nickel; 4.7% to 6% chromium; 2% to 3.25% titanium; up to 0.08% carbon; the percentage of nickel, titanium and carbon being such that

$$\text{Total Ni} - K(\text{Ti} - 4\times\text{C})$$

lies between 34.5% and 37.5%, and the percentage of chromium, titanium and carbon being such that

$$\text{Cr} + (\text{Ti} - 4\times\text{C})$$

lies between 7% and 8%, K being a constant having a value of about 2.4, and Ni, Cr, Ti and C being respectively nickel, chromium, titanium and carbon in weight percentage; and the balance being substantially all iron whereby a novel age hardened iron-nickel-chromium-titanium alloy is obtained having a unique combination of properties including the aforesaid temperature coefficient of modulus of elasticity having a small positive to negative value including zero together with high mechanical properties.

3. As an article of manufacture, a resilient element made of an age hardened iron-nickel-chromium-titanium alloy having the composition set forth in claim 1.

4. As an article of manufacture, a precision device including a resilient element made of an age hardened iron-nickel-chromium-titanium alloy having the composition set forth in claim 2.

5. As an article of manufacture, an age hardenable iron-nickel-chromium-titanium alloy possessing a temperature coefficient of modulus of elasticity having a small positive to negative value including zero and containing in weight percentage from 36% to 47% nickel; an effective amount up to 9% chromium; 1% to 4% titanium; up to 0.2% carbon; the percentage of nickel, titanium and carbon being such that

$$\text{Total Ni} - K(\text{Ti} - 4\times\text{C})$$

lies between 34.5% and 39%, and the percentage of chromium, titanium and carbon being such that

$$\text{Cr} + (\text{Ti} - 4\times\text{C})$$

lies betwen 4% and 9%, K being a constant having a value of about 2.4, and Ni, Cr, Ti and C being respectively nickel, chromium, titanium and carbon in weight percentage; and the balance being substantially all iron whereby a novel age hardenable iron-nickel-chromium-titanium alloy is obtained having in the aged condition a unique combination of properties, including the aforesaid temperature coefficient of modulus of elasticity having a small positive to negative value including zero together with high mechanical properties.

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CERTIFICATE OF CORRECTION.

Patent No. 2,266,482. December 16, 1941.

NORMAN B. PILLING, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 73, claim 1, for "2.4%" read --2.4--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of July, A. D. 1942.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)