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[54] **TIMEPIECE MAINSPRING OF COBALT-NICKEL BASE ALLOYS HAVING HIGH ELASTICITY AND HIGH PROPORTIONAL LIMIT**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 250,927, May 8, 1972, abandoned, which is a continuation-in-part of Ser. No. 876,551, Nov. 13, 1969, abandoned.

[52] **U.S. Cl.** ..... **148/11.5 F;** 75/170; 75/171; 148/12.7; 148/32; 148/32.5

[51] **Int. Cl.**[2] **C22C 19/07**

[58] **Field of Search** ..... 148/32, 32.5, 31, 2, 11.5 F, 148/12.7; 75/170, 171

[56] **References Cited**

UNITED STATES PATENTS

2,859,149 11/1958 Straumann 75/171

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[57] **ABSTRACT**

Timepiece mainsprings of cobalt-nickel base alloys containing chromium within a narrow range retain their high corrosion resistance, high elasticity, high proportional limit and substantial extensibility for long periods and through many cycles of winding and unwinding.

10 Claims, No Drawings

TIMEPIECE MAINSPRING OF COBALT-NICKEL BASE ALLOYS HAVING HIGH ELASTICITY AND HIGH PROPORTIONAL LIMIT

CROSS REFERENCE TO RELATED APPLICATION

This application is a Continuation-In-Part of our copending application Ser. No. 250,927, filed May 8, 1972, now abandoned the latter being a Continuation-In-Part of our now abandoned application Ser. No. 876,551 filed Nov. 13, 1969.

BACKGROUND OF THE INVENTION

In the materials conventionally used for springs, e.g. copper alloys such as beryllium copper alloys, titanium copper alloys and phosphor bronze alloys, iron alloys such as carbon alloys, the proportional limit σ is 120–140 kg/mm² at most. As a result, the value of the quantity σ^2/E, where E is Young's modulus, is relatively low. Of the materials mentioned, stainless steel and cobalt base alloys have the largest co-efficient of elasticity and proportional limit, but these materials suffer from the defects that they are not nonmagnetic and are extremely difficult to form into main springs.

Although cobalt-base alloys have been investigated, and are, in fact, in use as main springs, the conventional alloys do not possess the requisite qualities for the high level of performance desired.

In addition, it is necessary that an alloy designed for use in main springs of watches and other timepieces be workable. Workability is measured by susceptibility to cold rolling, cold drawing, hot forging, castability and weldability. Also, high tensile strength and high corrosion resistance are needed.

These properties being widely known, attempts have been made to improve the conventional cobalt base alloys by the addition of further elements. However, as the amount of additional elements used to this date has now approached the upper limit of solubility, further amounts of such elements cannot be added without seriously impairing the workability of the material and thereby rendering it commercially impracticable.

SUMMARY OF THE INVENTION

Alloys used in a timepiece mainspring in accordance with the present invention have the following composition, where the values given are in percentages by weight:

Co	30 – 50%
Ni	25 – 35%
Mn	up to 2%
Si	up to 1.5%

At least one of the following three elements in the range shown,

Cr	6 – 9%
Mo	8 – 12%
W	2 – 9% and preferably 2 – 6% where Cr + Mo + W totals 15 – 30%
Fe	up to 5%

and at least one of the following three elements in the range shown

Ti	0.05 – 5%
Nb	0.1 – 6%
Be	0.01 – 3%

To prepare the alloy having above compositions, the components listed are placed in a crucible and melted in a vacuum at a temperature between 1,400° and 1,600°C. After melting is complete, an ingot may be cast, which is then quenched at 1,100°– 1,200°C for 10–90 minutes. The alloy is cold-processed until the cross-sectional area is reduced by at least 80 percent. For maximum hardness the cold-processed material is age-hardened for 1–5 hours at 400°–600°C.

Accordingly, an object of the present invention is a mainspring which is corrosion resistant, has high elasticity, high proportional limit and long life.

A further object of the present invention is a timepiece mainspring of a group of improved alloys based on cobalt and nickel containing chromium lying within a restricted range.

Yet another object of the present invention is a process for manufacturing a timepiece mainspring having high corrosion resistance, high elasticity and high proportional limit.

An important object of the present invention is a process for treating an alloy based on cobalt and nickel and containing chromium lying within a restricted range and converting same into a mainspring for a timepiece.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The properties of the mainsprings of the present invention depend upon the composition of the alloys used and the way in which they respond to the processing involved. Insofar as the properties of the mainspring depend on the compositions, these properties may be presented in terms of the elements present.

1. Co, 30–50%; Ni, 25–35% (all quantities being by weight). Both Co and Ni are members of the iron group and as such have high strength. However, they are far superior to Fe in corrosion resistance over the entire range of temperatures at which the materials may be used. Ni has the further advantage that it increases the solubility of Periodic System Group No. 6 elements such as W and Mo which are introduced in order to increase toughness and workability of the alloy. Significant indices of workability are drawability and rollability. The quantity of Co and Ni used in any particular case depend on the required strength and toughness of the alloy.
2. At least one of the elements Cr, Mo and W, where Cr — Mo — W lies between 15 and 30 percent, Cr lies between 6 and 9 percent, Mo between 8 and 12 percent and W between 2 and 9 percent but preferably between 2 and 6 percent. Cr, Mo and W are all members of group 6 of the Periodic System and have the

capacity of improving the strength of metals in the iron group by dissolving in such metals. Cr is particularly effective in increasing corrosion resistance and for this reason is widely used in stainless steels. The contribution is strength made by the members of this group is as follows: W>Mo>>Cr, while in corrosion resistance the order is Cr>>Mo>W. To achieve high strength and elasticity, it is desirable to add as large a quantity as possible of W and Mo; however, in order to provide the requisite corrosion resistance Cr must be added and the amount of W and Mo is correspondingly reduced. As will become evident from data tabulated below, the optimum quantity of chromium lies between 6 and 9 percent, this quantity yielding a combination of properties not achieved when the chromium content is outside these limits.

With respect to the total quantity of Cr + Mo + W, where the total is less than 15% the increase in strength derived is inadequate, while if the total is more than about 30%, an intermetallic compound is precipitated and the workability of the alloy decreases as can be inferred from the solubility of the group 6 elements Co and Ni.

3. Mn less than 4 percent, Si less than 1.5%. Mn and Si are incorporated as deoxidation agents. They purify the alloy melt and indirectly increase the strength of products made from the alloys. Mn is completely soluble in Ni and Co. Consequently it is possible to add a large amount of Mn, but if this is done, the corrosion resistance of the resultant alloy is decreased. In fact, Mn has a deleterious effect on the corrosion resistance of the alloy even when added in quantities less than 4 percent.

Si in contrast to Mn is soluble in Ni and Co to the extent of less than 10 percent; consequently, if the quantity of Si added is too great the phase (Ni, Co) Si — intermetallic compound may be precipitated. Under such conditions, the alloy becomes unduly hard and difficult to work. Consequently, the quantity of Si added is less than 1.5 percent.

4. Ti 0.05 — 5%
   Nb 0.1 — 6%
   Be 0.01 — 3%

The elements Ti, Nb and Be when added in the ranges specified increase the age hardenability and the strength of the alloys in accordance with the present invention. It is believed that the age hardenability depends on the formation of compounds with nickel and cobalt as shown in Table 1.

TABLE 1

Additional Element	Intermetallic Compound	
Ti	Ni_3Ti,	Co_2Ti
Nb	$NbNi_3$,	$NbCo_2$
Be	BeCo,	BeNi

The lower limits of the ranges specified are based on the fact that quantities added in the amount below the lower limits have negligible effect in increasing the strength and age-hardenability of the material, while if added in quantities in excess of the upper limits, the product alloys become brittle and difficult to work. As is indicated in Table 1, the elements precipitate specific compounds. Consequently, if more than one of the elements of this group are added, no deleterious effect results.

5. Fe less than 5 percent. Fe is undesirable because of the fact that it decreases both the corrosion resistance and the strength of the resultant alloy. Where W and Mo are components of the alloy, it is desirable to have a minor quantity of Fe present. Also, it is frequently the case that up to about 4 percent of Fe may be present as an impurity. However, up to 4 percent of Fe may be included without appreciable degradation of the resultant alloy.

Carbon forms carbides and therefore hardens alloys. However, it reduces corrosion resistance and consequently it is desirable that the quantity of carbon present be kept as low as possible. However, as is the case with Fe in general it is impossible to avoid having some small quantity of carbon present. The amount should be kept to less than 0.5 percent at which level the effect of carbon may be disregarded.

A group of alloys in accordance with the present invention is shown in Table II.

Sample alloys shown in Table II were prepared by melting at 1,400°– 1,600°C in a high frequency induction vacuum furnace at a pressure of less than 1×10^{-2} mm Hg.

In the alloys of Table II, in proceeding from alloy A to alloy E, the cobalt composition drops from 49 to 30 percent while the nickel composition rises from 26 to 34 percent. Also, in all cases the sum of chromium plus molybdenum plus tungsten lies within the range of 15–30 percent and chromium itself lies within the range of 6–9 percent, molybdenum lies within the range of 8–12 percent and tungsten lies within the range of 2–9 percent.

TABLE II

Sample	A	B	C	D	E
Co	49	35	39	30	30
Ni	26	34	29	32	27
Mn	1	1.8	1.5	1	1.5
Si	0.3	1	1	1	1.3
Cr	9	7	6	7	8
Mo	8	11	12	11	8
W	2	—	5	4	9
Fe	1	4	4	3	4.5
Ti	2	3.2	—	5	4
Nb	1.7	—	1.0	3	6
Be	—	3	1.5	3	0.7

The tungsten was introduced as part of an alloy with iron. The other elements, in all cases were pure. The crucible used was made of alumina and after the basic elements were melted, Mn and Si were added to purify the molten materials. The melts were then poured into an ingot case made of cast-iron. The resultant ingots weighed about 2 kg. The ingots were then ground to render the surface smooth and subjected to hot forging and hot rolling. They were quenched at about 1,150°C through any temperature between 1,100° and 1,200° would be satisfactory, after which they were rolled to the desired thickness.

Quenching was carried out for between 10 and 90 minutes. During the cold-rolling subsequent to quenching, the cross-section of the ingot was reduced by at least 80 percent, this being a necessary step if the properties necessary for a mainspring are to be achieved.

Where the highest strength is desired, subsequent to cold-processing, the product is aged for 1–5 hours at between 400°C and 600°C.

Eduction is insufficient at temperatures below 400°C while at temperatures above 600°C the material becomes fragile. Where the aging is carried out for less than 1 hour the degree off age-hardening is inadequate, and where the aging is carried out for longer than 5 hours, the strength of the material is decreased. It is preferred that the aging process be held within the period of 2.5 to 3.5 hours while best results are obtained at close to 3 hours.

Mainsprings produced in accordance with the present invention are substantially superior to those of the conventional cobalt-based alloys with respect to mechanical strength. Looking at Table II again, it can be seen that the principle difference between the alloys of the present invention and the conventional alloys is in the reduced quantities of chromium and iron. Holding the chromium and iron within the limits specified increases both the workability and the corrosion resistance of the product alloys. Moreover, with reduced iron content, the quantity of chromium needed to provide the desired corrosion resistance may likewise be decreased, thus making it possible to increase the contents of tungsten and molybdenum, thereby increasing the strength of the product alloys. Mainsprings prepared as disclosed herein when immersed in artificial sweat, artificial seawater, dilute hydrochloric acid and dilute sulfuric acid for one month differ little in discoloration and corrosion from similar springs of conventional cobalt-based alloys.

Tests have shown that little increase in tensile strength, proportional limit or σ^2/E is achieved by increasing the chromium content of mainspring alloys beyond 9 percent. However, cold rollability, cold drawability, hot forgability, castability, and weldability all are impaired when the chromium content reaches 10%. Consequently a limit of 9 percent is set as the upper boundary for chromium.

The principle reason for holding the chromium content to a minimum of 6 percent is that at lower values, the corrosion resistance of the alloy is inadequate. Furthermore, fatique resistance is also seriously degraded at lower chromium contents.

Timepiece mainsprings made in accordance with the present invention are superior to mainsprings of conventional cobalt-based alloys in that the maximum torque is higher by about 15 percent. Furthermore, after fatigue tests consisting of 5,000 repeated windings and unwindings the decrease in torque is less than 5 percent. Consequently, it can confidently be stated that timepiece mainsprings prepared of alloys in accordance with the present invention are at least as good as those composed of conventional cobalt-based alloys with respect to mechanical properties.

The alloys of the present invention are non-magnetic, have high corrosion resistance, high elasticity, high proportional limit and high corrosion resistance as the result of minimizing the Fe content, increasing the Ni content and holding the Cr content within the range specified. Also, the inclusion of W and Mo as well as Cr from group 6 of the Periodic System increases the strength of the resultant alloy. Furthermore, it has been found that the alloys in accordance with the present invention maintain their superior properties including corrosion resistance as the temperature is raised. These properties are also characteristic of mainsprings of the alloys disclosed herein.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the article set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. A mainspring for a timepiece composed of an alloy consisting essentially of 30–50% Co, 25–35% Ni, at least one member selected from the group consisting of Cr in the range of 6–9 percent, Mo in the range of 8–12 percent, and W in the range of 2–9 percent, the total weight of Cr, Mo and W being in the range of 15–30 percent, at least one member selected from the group consisting of Ti in the range 0.05–5 percent, Nb in the range 0.1–6 percent and Be in the range 0.01–3 percent, less that 2% Mn, less than 1.5% Si and less than 5% Fe, said alloy having been quenched for 10–90 minutes from 1,100°–1,200°C, hot-forged, hot-rolled and cold-worked to reduce the cross-section of said alloy by at least 80 percent.

2. A mainspring as defined in claim **1** wherein the W content is in the range 2–6 percent.

3. The mainspring as defined in claim **1** wherein said alloy has been age-hardened for 1–5 hours at 400°–600°C.

4. The mainspring as defined in claim **2** wherein said mainspring has been age-hardened for 2.5–3.5 hours at 400°–600°C.

5. The mainspring as defined in claim **2** wherein said mainspring has been age-hardened for 3 hours at 400°–600°C.

6. The process of manufacturing a mainspring for a timepiece, comprising the steps of forming an alloy by melting in vacuum at a temperature between 1,400°C and 1,600°C a composition consisting essentially of 30–50% Co, 25–35% Ni, at least one member selected from the group consisting of Cr in the range of 6–9 percent, Mo in the range of 8–12 percent, and W in the range of 2–9 percent, the total weight of Cr, Mo and W being in the range 15–30 percent, at least one member selected from the group consisting of Ti in the range 0.05–5 percent, Nb in the range 0.1–6 percent and Be in the range 0.01–3 percent, less than 2% Mn, less than 1.5% Si and less than 5% Fe, quenching said alloy for 10–90 minutes from 1,100°–1,200°C hot-forging, hot-rolling and cold-processing said alloy to reduce the cross-sectional area by at least 80 percent.

7. The process as defined in claim **6,** wherein the W content of said alloy is in the range 2–6 percent.

8. The process as defined in claim **6,** further comprising the step of age-hardening said alloy for 1–5 hours at 400°–600°C.

9. The process as defined in claim **6,** wherein said alloy is age-hardened for 2.5–3.5 hours at 400°–600°C.

10. The process as defined in claim **6** wherein said alloy is age-hardened for 3 hours at 400°–600°C.

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