Patented Apr. 29, 1947

2,419,825

UNITED STATES PATENT OFFICE

2,419,825

COMPENSATING SPRING AND ALLOY FOR TIMEPIECES

Samuel Dinerstein, Delavan, Wis., assignor, by mesne assignments, to George W. Borg Corporation, Chicago, Ill., a corporation of Delaware

No Drawing. Application December 8, 1941, Serial No. 422,085

9 Claims. (Cl. 75—128)

1

The present invention relates in general to the so-called nickel iron alloys such as are used for the manufacture of hairsprings for watches and the like, and the principal object of the invention is to produce a new and improved alloy of this character.

The improvement is concerned mainly with the effect of temperature changes on the rate of oscillation of a balance wheel hairspring combination such as is used in a watch. In any hairspring, whether made of steel or one of the nickel iron alloys now commonly used for hairsprings, the increase in the width and length of a hairspring due to thermal expansion exactly balance each other and give rise to no change in rate due to change in temperature. The increase in the thickness of a hairspring due to thermal expansion increases the stiffness of the spring, and hence tends to increase the rate. This tendency is, however, counteracted by the increase in the inertia of the balance due to expansion, which tends to decrease the rate. In practice the increase in the thickness of the hairspring and the increase in the inertia of the balance can be made to approximately balance each other, and the total error due to thermal expansion is therefore very small.

The principal source of error is the change in the modulus of elasticity of the hairspring responsive to changes in temperature. The change is in a negative direction for steel and most alloys, which means that a hairspring grows weaker with a rise in temperature. Thus the negative thermal coefficient of elasticity causes a watch to run slower as the temperature rises. In the case of a watch having a steel hairspring, for example, the decrease in the rate is as much as four minutes per day for a rise in temperature of 50° F.

One method of correcting for the negative thermal coefficient of elasticity of the hairspring is to use a so-called compensating balance having a bi-metallic split rim which is effective to decrease the inertia of the balance as the temperature rises. A compensating balance gives excellent results insofar as timekeeping qualities are concerned, but is objectionable on account of the expense and for other reasons which are well understood.

With the discovery of the special properties of the nickel iron alloys a new method of eliminating the error due to negative thermal coefficient of elasticity was presented. The substantially pure nickel iron alloys have a thermal coefficient of elasticity which varies over a wide range with the amount of nickel used. By choosing the correct proportion of nickel to iron the thermal coefficient of elasticity can be made to equal zero, and there is even a limited range of nickel percentages which yield an alloy having a positive thermal coefficient of elasticity. A pure nickel iron alloy is not satisfactory for the manufacture of hairsprings, however. The alloy is too soft, for one thing, and the percentage of nickel which gives an alloy with a zero thermal coefficient of elasticity is too critical.

2

Various improvements have been made in the original nickel iron alloy to render it more suitable for hairsprings. For example, it has been found possible to at least partially overcome the objectionable softness of the alloy by adding small amounts of certain elements which function in known manner as hardening agents. It has also been discovered that the addition to a nickel iron alloy of a relatively large amount of chromium (10%, for example), changes the thermal coefficient of elasticity quite radically and produces an alloy which has a fairly uniform modulus of elasticity over a considerable temperature range. The alloy known as Elinvar is representative of the improved nickel iron alloys and contains about 8 to 12 parts of chromium, together with small amounts of tungsten, carbon, manganese and silicon which improve the working properties of the alloy and increase the elastic limit.

Hairsprings made of the nickel iron alloys are known as "compensating" hairsprings, although the thermal coefficient of elasticity is negative. They are, in, fact, compensating in the sense that the stiffness increases with increase in temperature and compensates for the increase in the inertia of the balance with increase in temperature. The increase in stiffness, however, is due to the increase in the thickness of the spring, rather than to a positive thermal coefficient of elasticity. No change in the modulus of elasticity is, in fact, required for compensation, and the ideal alloy would have a zero thermal coefficient of elasticity. That this is true will be perceived from consideration of a steel hairspring,

which is entirely satisfactory except for its large negative thermal coefficient of elasticity, which counteracts the effect of the increase in thickness of the spring with rise in temperature and prevents the latter change from effectively compensating for the increase in the inertia of the balance.

The best compensating hairsprings known prior to the present invention have a modulus of elasticity which is fairly constant over a temperature range extending from about 32° to 86° F. Inside this range the thermal coefficient of elasticity is about one-tenth that of steel, but it increases quite rapidly outside the range, resulting in large changes in rate.

A specific object of the invention may now be stated to be the production of an alloy in the nickel iron class from which hairsprings may be manufactured having a modulus of elasticity which is substantially constant over a much larger temperature range from −20° to +120° F., for example. Throughout this temperature range hairsprings made from my improved alloy have a thermal coefficient of elasticity which is equal or very nearly equal to zero.

Additional objects of the invention have to do with the production of an alloy of the above character from which hairsprings may be produced which are of superior hardness, stainless, and non-magnetic. The invention is also concerned with the method of manufacture whereby the properties of the alloy are preserved in the finished hairsprings.

A further object of the invention may therefore be stated to be the production of a hairspring for use in watches, measuring instruments and the like, which has physical and chemical properties which are necessary and desirable and which has in particular a modulus of elasticity which is substantially constant over a temperature range extending from −20° to +120° F.

In connection with the foregoing statements as to the objects of the invention, the further statement should be made that hairsprings from a given alloy, even from the same melt, vary somewhat in their properties and that the optimum results are attained only in the case of selected hairsprings. The average temperature range attained, while much greater than any range attained before, is somewhat narrower than the range given, which may be regarded as substantially the maximum range that may be expected.

My improved hairspring is made from an alloy having preferably the following composition:

	Per cent
Nickel	35.0
Chromium	9.0
Manganese	1.5
Silicon	1.0
Carbon	0.06
Tungsten	0.3
Calcium	0.1
Beryllium	0.5
Iron	The remainder

The components are weighed accurately to make up a lot of the desired size. A small lot is to be preferred, as this permits laboratory accuracy in the control of the composition of the alloy. The materials should be of the highest grade obtainable, substantially free of sulphur and phosphorus. The beryllium may be added in the form of a nickel beryllium alloy of known percentage composition, which reduces the amount of pure nickel required. Calcium may

be supplied in the form of a silicon calcium alloy, which similarly reduces the amount of pure silicon. The calcium acts as a scavenger in removing oxides and nitrides in known manner, and the indicated percentage is the residue remaining in the alloy after casting. The amount of this residue is not critical and could be less than indicated, although enough should be used to accomplish the desired result. The carbon content of the alloy is quite critical, and hence the carbon content of all the ingredients must be accurately known and as to the principal ingredients must be very low, due to the small percentage of carbon in the alloy. The carbon is preferably obtained by using the amount normally present in the nickel beryllium alloy, supplemented by the addition of chrome carbides. It will be understood from this that the chromium required is supplied in part in the form of chrome carbides of known composition or in the form of a ferro-chrome carbide. Some carbon is lost during melting of the alloy so enough should be used to make up for the loss. I have found that when the materials are melted as described hereinafter the specified percentage of .06 is obtained if the percentage calculated from the analysis and weight of the materials is approximately .1.

The various components are melted in a vacuum, employing a high frequency induction furnace of the type such as has been used heretofore in the melting of similar alloys. Melting in a vacuum prevents contamination from the air, which would tend to produce oxides and nitrides. The use of an induction furnace permits rapid melting and has the added advantage that the materials are rapidly stirred as soon as melted. To prevent contamination from the furnace lining, a special pre-formed Alundum lining is used. This lining should be heated in sulphur-free air to a temperature of 1800° F. to oxidize the small percentage of sulphur which is normally present.

The melting operation requires about three minutes, at the end of which a temperature of about 2700° F. is reached. This temperature is high enough to dissociate the chrome carbides and to melt all of the materials except the carbon and tungsten, which go into solution. The heating of the melt is continued a little longer, or until it reaches a temperature of approximately 2930° F., when it is ready for pouring.

The mold is preferably chilled and has a long, slender cavity adapted to produce an ingot of desirable shape for the production of wire. The size of the mold cavity may be ½ inch by 14 inches, for example. The molten alloy is poured into the mold very rapidly, and the metal solidifies almost as fast as it is poured. The total elapsed time for the complete pouring operation, including solidification of the ingot clear to the top should not exceed about one second. A high rate of solidification is very desirable, as it prevents segregation of the components due to the difference in their melting points and thus insures an ingot of uniform composition throughout. However, it is possible for solidification to take place too rapidly, resulting in what is known as secondary piping. I have found that very satisfactory results are secured if the melt is heated to about 2930° F., as previously mentioned, which insures that the ingot will solidify at the proper rate.

The mold described above is suitable for a one pound lot of material. If the alloy is made up in larger lots, a multiple-cavity mold may be used.

After removal from the mold the ingot is put through a hot working process, or preferably is given a heat treatment for about 48 hours in order to improve the ductility of the alloy and adapt it for cold working such as swaging and drawing.

After the heat treatment the ingot is finished off by a grinding operation, or by turning down in a lathe, in order to remove the somewhat rough exterior surface. It is then reduced to a wire of the correct size by successive swaging and drawing operations in known manner. The wire is then rolled into a ribbon of the desired shape.

During the reduction of the ingot to wire the material has to be annealed several times, which is accomplished by heating to the requisite high temperature and then quickly cooling by quenching in water. It is important that these operations be performed carefully and in the same way each time, and it is of particular importance that the alloy be always heated to approximately the same temperature. I have ascertained that excellent results are secured by heating to a temperature of 2060° F. The necessity for the exercise of care in the annealing operations arises out of the fact that the different chrome carbides formed as the result of heating to different temperatures have a considerable effect on the properties of the alloy. By annealing the alloy as described, uniform and advantageous carbide formations are obtained.

In further explanation of the foregoing, it may be stated that the changes in chrome carbide formation take place mainly in the temperature range extending from about 1340° F. to about 1700° F. Within this temperature range the carbides are continually changing. If the alloy is quenched from a temperature within the range stated, the results are uncertain and variable, but if the alloy is always heated above the critical temperature of 1700° F., and is rapidly cooled through the range 1700° F.–1340° F., the carbides which are precipitated in the cold metal are always the same. It is desirable to quench the alloy from a still higher temperature, but there is an upper limit imposed by the fact that if the annealing temperature is somewhat higher than 2060° F. the beryllium has a tendency to form large, brittle crystals which cause the wire to break during drawing. The upper temperature limit is somewhat different if other hardening agents are used.

If hairsprings for watches are to be made, lengths of the ribbon which are sufficient for the desired springs are cut off and are coiled into flat spirals to form the springs, which are set and hardened by a heat treatment. The hardening is thus effected by the so-called precipitation hardening process rather than by cold working. The finished springs have substantially the same hardness, or elastic limit, as steel springs, and in this respect are superior to other springs made of nickel iron alloys.

In connection with the hardening of the springs, it should be mentioned that the heat treatment is carried out at a temperature which is below the temperature range in which changes in the carbides take place, and consequently the latter are not affected. A suitable heat treatment which may be cited as an example continues for five minutes at a temperature of 1250° F. and is effective to completely precipitate the beryllium.

The manganese and silicon are included in the

alloy mainly to improve its characteristics as regards ductility and malleability, and function in known manner. The amounts to be used are not critical and may vary from .2 to 3 per cent of manganese and from .2 to 1 percent of silicon.

The tungsten increases the toughness of the alloy in known manner. I have ascertained also that the tungsten is of value in maintaining a uniform modulus of elasticity in the upper part of the temperature range. The amount used may range from .2 to 1 per cent. The tungsten may be replaced by molybdenum, for example, which has a similar effect on the alloy.

The quantity of beryllium used may range from .2 per cent to about 1 per cent. This is the component of the alloy which renders it susceptible to hardening by the precipitation hardening process. Aluminum, zirconium, or titanium may be used for the same purpose. The residue of calcium which is present in the alloy is also believed to have some effect in promoting the hardening process, although it is mainly added for a different purpose, as previously mentioned.

The amount of nickel used may vary between 30% and 40%, and the chromium between 5% and 10%. The nickel functions in the same general way as heretofore in nickel iron alloys. The chromium is the component which is responsible for the uniform modulus of elasticity characteristic of the alloy. Its action is considerably modified, however, by the chrome carbides which are present.

I attribute the greatly increased range over which a substantially uniform modulus of elasticity is secured to the presence of the proper amount of tungsten or equivalent metal and to the presence of a very small but carefully regulated amount of carbon. All of the carbon which is contained in the alloy is believed to be present in the form of one or more chrome carbides, the exact composition having not as yet been determined. It is known, however, that chrome carbides change during heating and cooling, as heretofore explained, and I have ascertained that if the annealing of my alloy is not carried out properly, its desirable characteristics are to a considerable extent destroyed. It may be concluded from these facts, not only that the carbon is present in the form of one or more chrome carbides, but that the composition of the carbides is of importance in attaining the desired results. The proper carbide structure is obtained by carrying out the annealing operations in the prescribed manner.

A watch equipped with a hairspring manufactured from my improved alloy has a nearly constant rate over a temperature range from −20° to +120° F. The No. 1 grade of Elinvar hairsprings, which are the best prior art hairsprings on the market, so far as known, are guaranteed to give a rate variation not greater than ½ second per degree change in temperature over a range from 0° to 34° C., or 32° to 93.2° F. Outside this range they are not guaranteed at all, and in fact give rates which change very rapidly with changes in temperature. Hairsprings made of my improved alloy have an accurate working temperature range, therefore, which is more than double the range claimed for the Elinvar springs.

The range is in fact much wider than is usually considered necessary in the case of hairsprings for watches, which are not often subjected to such great temperature changes. There are situations, however, where the wide range is necessary. In the case of hairsprings for mechanical or clock-

work type fuses, for example, the wide range is essential, and applicant's alloy is believed to be the only alloy from which springs can be manufactured which will meet the requirements.

The invention having been described, that which is believed to be new and for which the protection of Letters Patent is desired will be pointed out in the appended claims.

I claim:

1. A stainless spring having a high elastic limit and a substantially constant modulus of elasticity over a temperature range of more than 110° F., made from an alloy containing about 35 per cent nickel, 9 per cent chromium, 1.5 per cent manganese, 1 per cent silicon, .3 per cent tungsten, .06 per cent carbon in the form of chrome carbide, .5 per cent beryllium, a trace of calcium and the remainder iron, said alloy having been repeatedly annealed in the fabrication of the spring therefrom, each annealing operation comprising heating to a temperature above the temperature range in which changes in chrome carbide structure take place and rapid cooling by quenching, and the spring having been hardened by precipitation of the beryllium during a heat treatment carried out at a temperature below the temperature range in which changes in chrome carbide structure take place.

2. A spring having a high elastic limit and a substantially constant modulus of elasticity over a wide temperature range and containing 30 to 40 per cent nickel, 5 to 10 per cent chromium, small amounts of manganese and silicon, .2 to 1 per cent of tungsten, not more than .06 per cent nor less than .04 per cent of carbon in the form of chrome carbides produced by repeated annealing operations at a temperature above a critical temperature of approximately 1700° F., each annealing operation being followed by quenching the alloy to cool it rapidly, not more than 2 per cent of beryllium precipitated by a heat treatment to harden the spring, the heat treatment being carried out at a temperature which is below 1340° F., and the balance substantially all iron.

3. A spring having a high elastic limit and a substantially constant modulus of elasticity over a wide temperature range, and made from a nickel-iron-chromium alloy containing also small amounts of manganese, silicon, tungsten, beryllium, and a regulated amount of carbon not greater than .06 per cent nor less than .04 per cent by weight, the said carbon being in the form of carbides which result from rapidly cooling the alloy by quenching from a temperature above the temperature range in which changes in carbide structure take place, and the said spring being hardened by precipitation of the beryllium during a heat treatment carried out at a temperature below the temperature range in which changes in chrome carbide structure take place.

4. A soft wire or ribbon for use in the manufacture of springs, said wire being produced with the aid of drawing operations from an alloy containing 30 to 40 per cent nickel, 5 to 10 per cent chromium, .2 to 3 per cent manganese, .2 to 1 per cent silicon, .2 to 1 per cent tungsten, .04 to .06 per cent carbon, .2 to 1 per cent beryllium, and the balance substantially all iron, the said carbon content being in the form of carbides such as result from annealing operations following the drawing operations, each annealing operation comprising heating the alloy to a temperature above the temperature range in which changes in carbide structure take place and rapidly cooling the alloy by quenching, and the said beryllium content being in solid solution.

5. The method of securing and maintaining advantageous chrome carbide formation in a precipitation hardened spring made from an iron nickel chromium alloy, said alloy containing beryllium as a hardening agent, which consists in regulating the amount of carbon in the alloy to a value of approximately .06 per cent of the whole by weight, repeatedly annealing the alloy during manufacture of the spring by heating and quenching, the temperature of heating being above the temperature range in which changes in chrome carbide structure take place, and hardening the spring by a heat treatment carried out at a temperature which is below said temperature range to precipitate the hardening agent without affecting the chrome carbide formation.

6. The method of utilizing carbon in an iron nickel chromium alloy to increase the temperature range in which springs made from such alloy have a substantially constant modulus of elasticity, said alloy containing a precipitation hardening agent and the manufacture of said springs including a plurality of drawing operations followed by annealing operations, which includes the steps of regulating the amount of carbon in the alloy to a value between about .04 per cent and .06 per cent which results in chrome carbide formation having the desired effect on the properties of the alloy in increasing said temperature range, in conducting the annealing operations which are performed on the alloy during the fabrication of the springs at a temperature which is higher than the temperature range in which changes in chrome carbide structure takes place, and in rapidly cooling the alloy by quenching after each annealing operation, whereby the desired chrome carbide structure is retained.

7. The method of manufacturing a soft wire for use in the manufacture of springs having a high elastic limit and a substantially constant modulus of elasticity over a wide temperature range, which consists in preparing an alloy containing 30 to 40 per cent nickel, 5 to 10 per cent chromium, .2 to 3 per cent manganese, .2 to 1, per cent silicon, .2 to 1 per cent of a metal from the group comprising tungsten and molybdenum, 0.4 to .06 per cent carbon combined with a part of said chromium in the form of chrome carbides, .2 to 1 per cent beryllium, and the balance substantially all iron, in forming rods from said alloy, in reducing said rods to wire by successive drawing operations, in annealing said alloy a plurality of times during tis reduction from rods to wire, whereby at least the major part of the hardness imparted by the drawing operations is destroyed, and in producing uniform chrome carbide formations in the finished wire by conducting said annealing operations at a temperature above the temperature range in which changes in chrome carbide formations take place and by rapidly cooling the alloy by quenching after each annealing operation.

8. An alloy for use in the manufacture of hairsprings having a substantially constant modulus of elasticity over a temperature range of more than 100° F., the lower limit of said range being below 0° F., said alloy containing 30 to 40 per cent nickel, 5 to 10 per cent chromium, .2 to 3 per cent manganese, .2 to 1 per cent silicon, .2 to 1 per cent of a metal from the group of metals which includes tungsten and molybdenum, .04 to .06 per cent of carbon, and .2 to 1 per cent of a precipitation hardening agent from the group com-

prising beryllium, aluminum, zirconium and titanium, and the balance being substantially all iron.

9. A spring having a substantially constant modulus of elasticity over a temperature range of more than 100° F., the lower limit of said range being below 0° F., made from an alloy containing 30 to 40 per cent nickel, 5 to 10 per cent chromium, .2 to 3 per cent manganese, .2 to 1 per cent silicon, .2 to 1 per cent of a metal from the group comprising tungsten and molybdenum, .04 to .06 per cent of carbon, a precipitation hardening agent, and the balance substantially all iron, said spring having been repeatedly annealed during fabrication from said alloy and hardened by a heat treatment resulting in the precipitation of said hardening agent.

SAMUEL DINERSTEIN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,945,653	Masing	Feb. 6, 1934
2,266,482	Pilling	Dec. 16, 1941
2,174,171	Wasson	Sept. 26, 1939
1,675,644	Dean	July 3, 1928

OTHER REFERENCES

M. F. Sayre and A. V. de Forest: New Spring Formulas and New Materials in Precision Spring Scale Design, contributed by the Research Committee on Mechanical Springs for presentation at the annual meeting, New York, N. Y., Dec. 3 to 6, 1934, of the American Society of Mechanical Engineers, 15 pp. See especially pp. 1, 3, 5 (copy in Division 3, 148/21.55).