

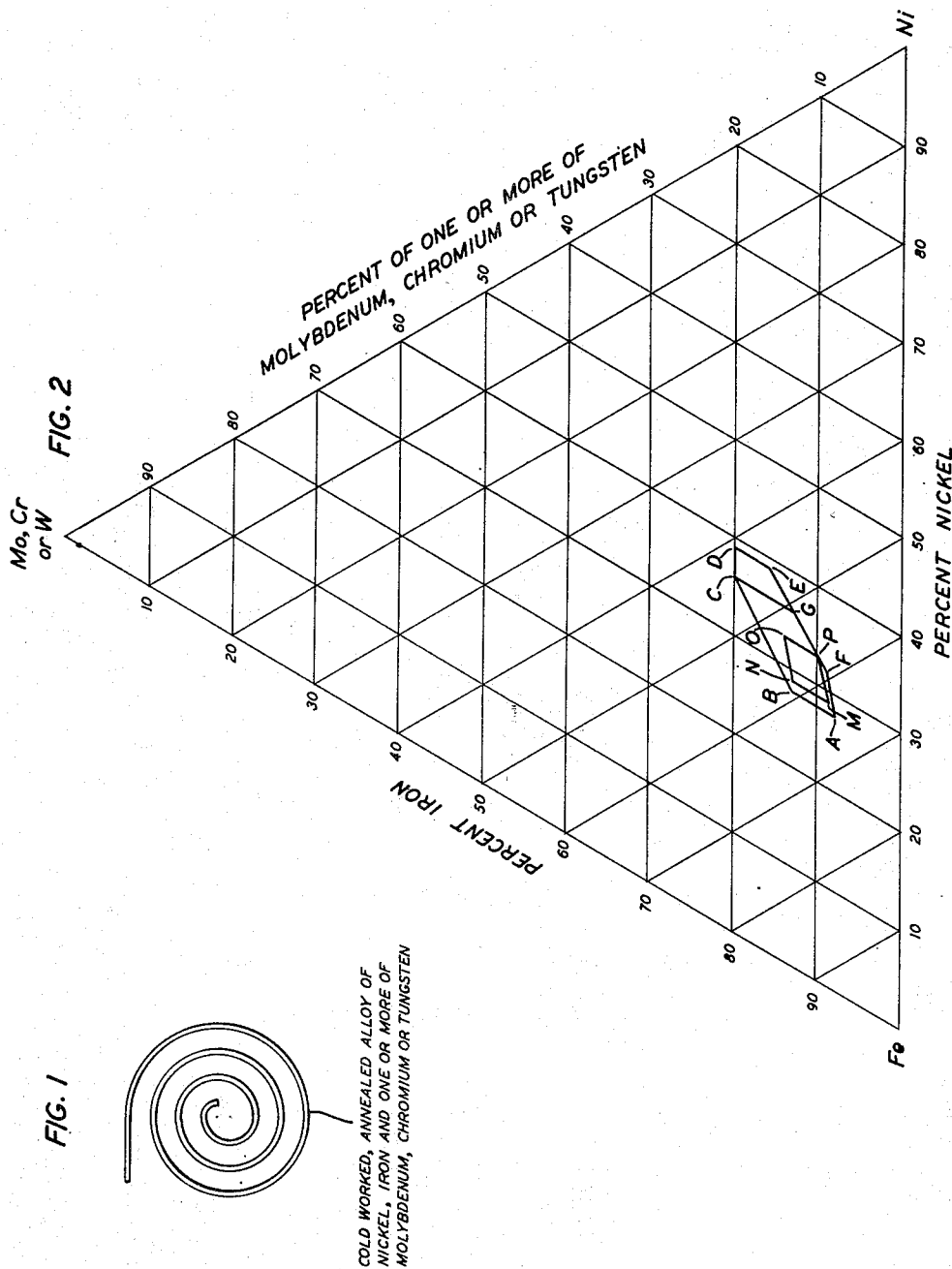
Dec. 25, 1956

M. E. FINE

2,775,536

BODIES HAVING LOW TEMPERATURE COEFFICIENTS OF ELASTICITY

Filed July 19, 1952



INVENTOR
M. E. FINE
BY
Edwin B. Cave
ATTORNEY

1

2,775,536

BODIES HAVING LOW TEMPERATURE
COEFFICIENTS OF ELASTICITY

Morris E. Fine, Morristown, N. J., assignor to Bell Tele-
phone Laboratories, Incorporated, New York, N. Y., a
corporation of New York

Application July 19, 1952, Serial No. 299,909

2 Claims. (Cl. 148—11.5)

This invention relates to metal alloys, and bodies formed therefrom, the modulus of which varies but little over a wide temperature range, to devices which function through the elastic distortion of such bodies, and to the process of forming said metal alloys.

When devices which function through the elastic distortion of metal members, such as spiral hair springs for watches and clocks, springs for measuring or applying force or mechanical vibratory elements, such as vibrating reeds or tuning forks, are designed to operate under varying temperature conditions, and when it is required that the operating characteristics of these devices be essentially constant under these varying conditions, it is necessary that the metal member be a body which exhibits as little change in modulus of elasticity as possible over the entire temperature range to which the device may be subjected.

Although alloys are known to the art which have zero temperature coefficients of modulus of elasticity in the vicinity of room temperature and which have low temperature coefficients over a substantial temperature range, these alloys are all ferromagnetic and possess relatively high saturation magnetizations. For many purposes, it is desirable that the ferromagnetism of elements functioning through elastic distortion be minimized in so far as possible.

The known alloys of zero temperature coefficient at room temperature are alloys which exhibit a minimum point, at room temperature, on their curves of modulus of elasticity versus temperature. At this minimum point, the modulus does not change with temperature and, therefore, the temperature coefficient is zero. One such alloy is a binary iron-nickel alloy containing in the vicinity of 45 percent nickel. An improvement in alloys of this type is described and claimed in United States Patent 2,561,732, issued July 24, 1951, to the present applicant. According to that patent, the curve in the vicinity of the minimum point, for this alloy and for related iron-nickel-molybdenum alloys, is made as shallow as possible by composition control and by subjecting the alloy to cold working. The shallower the curve on either side of the minimum point, the wider is the temperature range over which the temperature coefficient maintains a low value.

The present invention is based on the fact that these and similar alloys also exhibit a maximum point on their curves of modulus versus temperature, this maximum point occurring just below the Curie temperature and at a substantially higher temperature than the minimum point. The maximum point on the curve is also a point at which the modulus does not change with temperature and at which the temperature coefficient is therefore zero. The proximity of the maximum point to the Curie temperature results in a relatively low saturation magnetization at the maximum point although the alloy is still ferromagnetic.

According to the present invention, alloy compositions are chosen which lower this maximum point, together with the Curie temperature, to a temperature in the vicinity of room temperature, as for instance between 0°

2

C. and 50° C. or preferably between 15° and 35° C. or near the center of the operating temperature range of the element or device formed from the alloy. As was true of the mainimum point referred to above, the curve in the vicinity of the maximum point is made flatter (and the low temperature coefficient spread over a wider temperature range) by cold working of the alloys. As a result, alloys are obtained which have low saturation magnetizations and which have low temperature coefficients of modulus of elasticity over a substantial temperature range including room temperature.

The alloys of the present invention are formed of iron, nickel and one or more of the metals molybdenum, chromium and tungsten, with or without added modifying ingredients, as will be discussed below. These alloys are suitable for the purposes of the present invention if they are proportioned so that their compositions fall within a particular area on a triaxial diagram the three coordinates of which are weight percent nickel, weight percent iron and weight percent of at least one metal selected from the group consisting of molybdenum, chromium and tungsten. The range of compositions of the alloys useful for the purposes of the present invention is shown in the accompanying drawing in which:

Fig. 1 is a plan view of a spiral spring formed according to the present invention; and

Fig. 2 is a triaxial diagram, the three coordinates of which are weight percent nickel, weight percent iron and weight percent of at least one metal selected from the group consisting of molybdenum, chromium and tungsten.

The spiral spring of Fig. 1 is formed of an iron-nickel-molybdenum alloy, the proportions of which fall within the limits defined below, said alloy having been cold worked and then annealed, as set forth below, so as to impart to it a very low temperature coefficient of modulus of elasticity over a broad temperature range. This property of the spring, together with the low saturation magnetization of the alloy, renders it well adapted for use as the balance spring of a watch or clock.

In Fig. 2 is shown the area defining the limits of the relative proportions of the three ingredients, iron, nickel and one element of the group molybdenum, chromium and tungsten in alloys suitable for the present invention. This area is bounded by the hexagon formed by straight lines joining successively the points represented by the following compositions:

Point	Composition (percent)		
	Ni	Mo, Cr, W	Fe
A	28	8	64
B	28	13	59
C	36	20	44
D	39	20	41
E	39	16	45
F	32	9	59

Preferably the alloy compositions fall within the pentagon formed by straight lines joining successively the points represented by the following compositions:

Point	Composition (percent)		
	Ni	Mo, Cr, W	Fe
A	28	8	64
B	28	13	59
C	36	20	44
G	36	13	51
F	32	9	59

More preferably, the alloy compositions fall within the quadrangle formed by straight lines joining successively the points represented by the following compositions:

Point	Composition (percent)		
	Ni	Mo, Cr, W	Fe
M-----	29	8.5	62.5
N-----	29	13	58
O-----	33	14	53
P-----	33	10	57

With alloys falling within the areas defined above, the proportion of molybdenum or chromium preferably should not exceed 13 percent by weight of the alloy, since larger amounts may tend to segregate and form a second phase. Larger proportions of combinations of these elements, such as molybdenum and chromium, molybdenum and tungsten, chromium and tungsten, and molybdenum, chromium and tungsten, may be employed within the limits defined by the areas referred to above.

When the alloys are ternary iron-nickel-molybdenum alloys, to which modifying ingredients may be added as will be discussed below, the relative proportions of the three basic ingredients preferably fall within the limits of 8.5 percent to 11 percent molybdenum, 29 percent to 31 percent nickel and the remainder iron.

In the alloys of the present invention, the Curie point and the point of maximum modulus (zero temperature coefficient) are shifted to a lower temperature with decreasing nickel content and with increasing content of one or more of molybdenum, chromium and tungsten. Therefore, by control of the relative proportions of nickel to molybdenum, chromium and tungsten, the point of zero temperature coefficient, associated with maximum modulus, can be caused to occur at the desired temperature.

In order to maintain a low temperature coefficient over a wide temperature range, it is desirable that the curve of modulus versus temperature be as flat as possible in the vicinity of maximum modulus, as discussed above. The greater the nickel to iron ratio in the alloy, the flatter is the curve. Therefore it is desirable that as high a nickel content as possible be used, consistent with obtaining the point of maximum modulus at the required temperature.

As indicated above, the curve is also made flatter by cold working of the alloy. This treatment is carried out on the alloys by first subjecting them to a cold working operation, such as swaging, rolling, drawing or the like, which reduces their cross-sectional area and then subjecting them to a low temperature anneal at a temperature substantially above any temperature to which the bodies may be expected to be exposed during their normal operation. The area reduction induced by cold working should be at least 3 percent and preferably at least 5 percent in order to have the required effect upon the alloy. The upper limit to the amount of cold reduction is set only by the amount to which the alloy can be subjected without fracture. This cold working results potentially in the required broadening of the low temperature coefficient of modulus of elasticity of the alloys referred to above over the broad temperature range referred to above.

However, in this cold worked state the modulus of elasticity will be altered by a change in the crystalline condition of the alloy as the temperature is raised above that at which the cold working took place. In order to stabilize the alloy against such a change in modulus it is necessary to anneal it at a temperature above that to which the alloy will be subjected during its normal operation but below the temperature for full recrystallization of the alloy. Therefore, with an operating range up to 50° C., it is necessary that the cold worked body be annealed at a temperature substantially above 50° C., such as 100° C. or 150° C. Ordinarily this annealing will take place in the

range of 200° C. to 750° C., or preferably in the range of 300° C. to 600° C., in order to provide a safe margin for most operating ranges. A convenient annealing temperature which yields good results is 400° C. The annealing time is not critical, it being necessary only that all parts of the body be allowed to reach the annealing temperature. A convenient annealing time is from one hour to five hours.

The alloys above have been described as composed of iron, nickel and one or more of the elements molybdenum, chromium and tungsten. To these basic alloys may be added certain modifying ingredients, in total amount up to 10 percent or more preferably up to about 5 percent, which may alter the other properties of the alloys or which may serve as diluents but which do not have a substantial effect upon the change of modulus of elasticity with temperature. Thus, up to 2 percent manganese may be added to improve the working properties of the alloys. Preferably between .25 percent and 1 percent of manganese is present for this purpose. Up to .25 percent carbon, up to 6 percent aluminum and up to 5 percent silicon may be present in the alloys and serve to harden them as well as having minor effects on certain other properties. Incidental impurities which have no effect upon the modulus of elasticity may also be present, though in total amount less than 2 percent and preferably less than 1 percent.

A particularly suitable alloy body was prepared having a composition of 10 percent molybdenum, 30 percent nickel, .75 percent manganese and the remainder iron together with incidental impurities. This alloy, when cold-rolled to an area reduction of 56 percent and annealed at 400° C. possessed a Curie point at about 85° C. and exhibited a variation of modulus of elasticity of less than 0.1 percent from its value at 25° C. over the temperature range between 0° C. and 50° C. At 25° C., the saturation magnetization of the alloy was 300 gauss. Over the temperature range of 0° C. to 50° C., the saturation magnetization varied from 600 gauss to 200 gauss.

Other desirable alloys possessing comparable properties after similar treatment are an alloy of 11 percent tungsten, 35 percent nickel, .75 percent manganese, and the remainder iron together with incidental impurities; an alloy of 12 percent chromium, 34 percent nickel, .75 percent manganese and the remainder iron together with incidental impurities; and an alloy of 8 percent molybdenum, 4 percent chromium, 33 percent nickel, .75 percent manganese and the remainder iron together with incidental impurities.

Treatment within the range of conditions set forth above, when applied to the range of alloys described above results in bodies having a modulus of elasticity which varies by not more than .5 percent, or by not more than .25 percent within the quadrangle above, over the range of 0° C. to 50° C. By a selection of alloy compositions and conditions of treatment within this range, considerably smaller changes in modulus can be achieved.

The invention has been described in terms of its specific embodiments and, since certain modifications and equivalents may be apparent to those skilled in the art, these embodiments are to be considered illustrative of, but not necessarily to constitute a limitation upon, the scope of the invention.

What is claimed is:

1. A metal element which functions through elastic distortion comprising a body of an alloy annealed, at a temperature between 150° C. and 600° C., from a cold worked state produced by subjecting said body to a cold area reduction of at least 3 percent, said alloy consisting of a composition defined within an area on a ternary diagram having as its coordinates, weight percent iron, weight percent nickel and weight percent of at least one element selected from the group consisting of molybdenum, chromium and tungsten, said area being defined

5

by a hexagon having as its corners the six points defined by (1) 28 percent nickel, 64 percent iron and 8 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (2) 28 percent nickel, 59 percent iron and 13 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (3) 36 percent nickel, 44 percent iron and 20 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (4) 39 percent nickel, 41 percent iron and 20 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (5) 39 percent nickel, 45 percent iron and 16 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; and (6) 32 percent nickel, 59 percent iron and 9 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; the amount of said component selected from the group consisting of molybdenum, chromium and tungsten being not greater than 13 percent when said component consists of molybdenum, and not greater than 13 percent when said component consists of chromium; and in addition to said composition up to 0.25 percent carbon, up to 2 percent manganese, and up to 5 percent silicon together with incidental impurities having no effect on the modulus of elasticity.

2. The method which comprises cold-working an alloy to achieve a cold area reduction of at least 3 percent and annealing said alloy from the cold-worked state at a temperature between 150° and 600° C., said cold-worked and annealed alloy consisting of a composition defined within an area on a ternary diagram having as its coordinates, weight percent iron, weight percent nickel and weight percent of at least one element selected from the group consisting of molybdenum, chromium and tungsten, said area being defined by a hexagon having at its corners the six points defined by (1) 28 percent

6

nickel, 64 percent iron and 8 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (2) 28 percent nickel, 59 percent iron and 13 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (3) 36 percent nickel, 44 percent iron and 20 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (4) 39 percent nickel, 41 percent iron and 20 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; (5) 39 percent nickel, 45 percent iron and 16 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten; and (6) 32 percent nickel, 59 percent iron and 9 percent of at least one of said elements selected from the group consisting of molybdenum, chromium and tungsten, the amount of said component selected from the group consisting of molybdenum, chromium and tungsten being not greater than 13 percent when said component consists of molybdenum and not greater than 13 percent when said component consists of chromium; and in addition to said composition up to .25 percent carbon, up to 2 percent manganese, and up to 5 percent silicon together with incidental impurities having no effect on the modulus of elasticity.

References Cited in the file of this patent

UNITED STATES PATENTS

1,652,556	Brace	Dec. 13, 1927
1,974,695	Straumann	Sept. 25, 1934
2,419,825	Dinnerstein	Apr. 29, 1947
2,524,660	Harder	Oct. 3, 1950

FOREIGN PATENTS

578,559	Great Britain	July 3, 1946
522,280	Germany	May 6, 1931