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Steinemann

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[54] **STRAINABLE MEMBERS EXPOSED TO TEMPERATURE VARIATIONS AND MATERIALS THEREFOR**

[75] Inventor: **Samuel Steinemann**, 4410 Liestal, Switzerland

[73] Assignee: **Institut Dr. Ing. Reinhard Straumann A.G.**, Waldenburg, Switzerland

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 728,422, May 13, 1968, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**..**267/182**

[51] **Int. Cl.** **F16f 1/04**

[58] **Field of Search**......................................267/182

[56] **References Cited**

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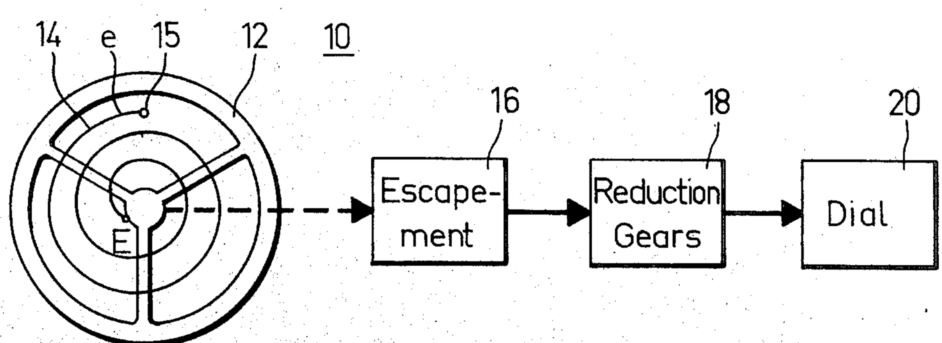
Primary Examiner—James B. Marbert

Attorney—Toren & McGeady

[57] **ABSTRACT**

A temperature-stable strainable member is formed of an antiferromagnetic alloy having a low temperature-coefficient of the modulus of elasticity. The member may be embodied in a mechanical oscillator as a vibratory element with a modulus of elasticity whose temperature coefficient is between $-10 \cdot 10^{-5}$ and $+10 \cdot 10^{-5}$ centigrade and which is composed of 20 – 29 percent manganese, 2 – 9 percent chromium, 0.03 – 1 percent carbon, the remainder iron with ordinary impurities less than 1 percent.

23 Claims, 5 Drawing Figures



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2 Sheets-Sheet 1

Fig. 1

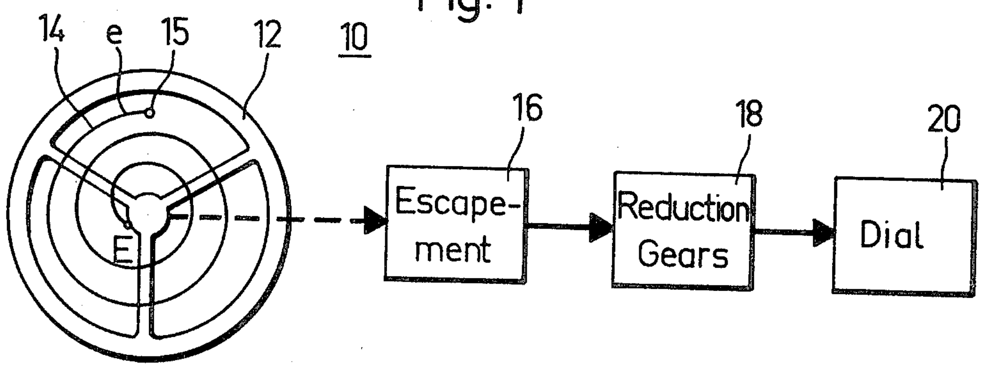
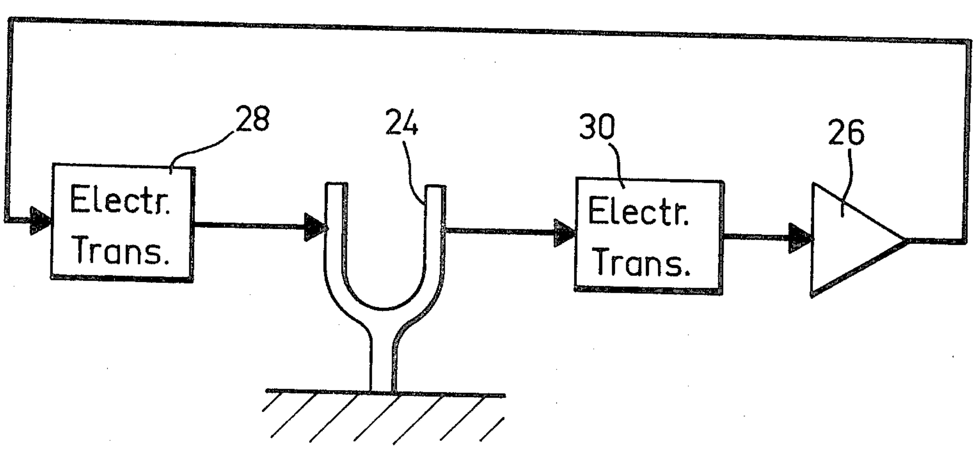


Fig. 2



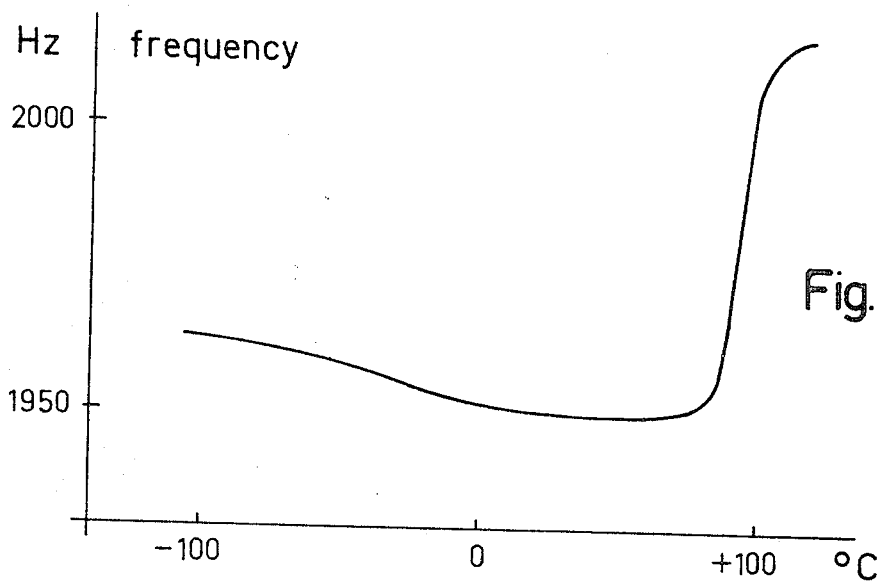


Fig. 3

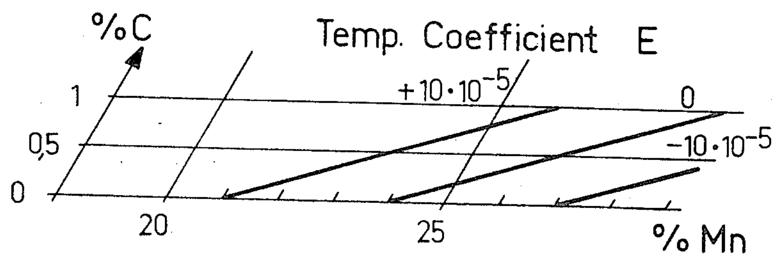


Fig. 4

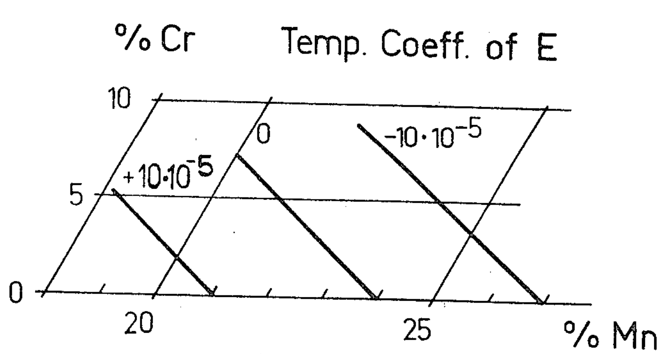


Fig. 5

STRAINABLE MEMBERS EXPOSED TO TEMPERATURE VARIATIONS AND MATERIALS THEREFOR

REFERENCE TO RELATED CO-PENDING APPLICATIONS

This application is a continuation-in-part of the co-pending parent application Ser. No. 728,422, filed May 13, 1968, and now abandoned by Samuel Steinemann and assigned to the same assignee as the present application.

BACKGROUND OF THE INVENTION

This invention relates to elastically strainable mechanical members, and materials therefor, and particularly to such members whose rate or extent of departure from the unstrained state in response to stresses must remain accurately consistent despite changes in temperature. The invention has special relevance to elastic members in mechanical oscillators whose frequency must remain temperature-stable so they can be used in instruments such as watches or mechanically resonant filters.

For many applications were accuracy is demanded, it is essential that mechanical members under repeated strain exhibit a substantially constant or otherwise reliable rate or extent of departure from the unstrained condition. For example, oscillating mechanical members, such as those used in mechanical resonators as tuning forks, or as resonators in electromechanical filters or other instruments, must exhibit an oscillatory frequency that remains substantially constant in response to changes in temperature. Such freedom from temperature effects is necessary for accuracy and stability in time pieces and other instruments.

Oscillating systems of watches, mechanical resonators such as tuning forks, electromechanical filters and other instruments etc., use so-called thermocompensating alloys, which are intended to eliminate temperature effects on the elasticity or frequency of oscillation. Ordinary structural materials, such as aluminum, copper and their alloys, steels etc., have negative temperature coefficients of elasticity of about $20 \cdot 10^{-5}$ per degree Centigrade or more. In thermocompensating alloys, the temperature effects are reduced to lower values of the order of $10 \cdot 10^{-5}$ per degree Centigrade, and possibly displaced to zero or even to positive values (note that a temperature coefficient $1/M \cdot dM/dT$ of elastic modulus of $10 \cdot 10^{116\ 5}$ corresponds to a rate of 4.3 sec/day of a watch).

In most resonant systems, a resonant frequency is determined not solely by the thermoelastic coefficient of the elastic member, but also by its thermal expansion and the thermal expansion of the masses or of all components of the oscillating system together. For example, a material, which as a rod for flexural oscillations has a neglibly small temperature coefficient of frequency will have a negative frequency dependence when incorporated as a spiral spring and coupled to the balance wheel in a watch; in the latter case, a positive thermoelastic coefficient must be attained by alteration of the alloy composition or different manufacture procedure. Different requirements occur in oscillating systems and instruments and cause different moduli to be decisive; such as for example the modulus of elasticity in spiral springs for watches and instruments, tuning

forks, electromechanical filters, spiral springs for instruments, the shear modulus for suspensions in instruments, cylindrically wound tension springs or compression springs, torsional oscillators, electromechanical filters, and also combinations of these two moduli; even the modulus of compression may become significant. Because of the temperature dependence of the Poisson Number connecting these moduli, the material has to be adapted to each application.

In addition to the requirements in respect of elasticity, these materials are also required to have low mechanical losses, good workability, corrosion-resistance, and high mechanical stability.

The conventional thermocompensating alloys, known under Trade Marks such as Nivarox, Ni-Span C, Isoval, are all based on ferromagnetic phenomena. Apart from the purely elastic Hooke's extension under load, an additional magnetostrictive extension occurs and the overall effect corresponds to a lowering of the modulus of elasticity. The process is called ΔE-effect or ΔEγ-effect, according to whether shape magnetostriction or volume magnetostriction pre-dominates. For temperature compensation, the decrease of magnetostriction towards the Curie-temperature is used and the alloy formation and treatment of these materials is virtually a formulation of magnetic and magnetomechanical properties. The effects are known in nickel, cobalt, iron-nickel-chrome alloys, iron-cobalt-chrome alloys, and iron-cobalt-nickel alloys, in which the temperature compensation of the elasticity is then achieved over ranges of temperatures of up to several 100°.

However, these ferromagnetic thermocompensating alloys are sensitive to external magnetic fields because of their basic operation. On magnetic saturation by an external field, the ΔE-effect disappears, for example, in nickel and with alloys withΔEγ-effect, the frequencies of an oscillator shift up to an order of magnitude of $10^{116\ 3}$ and the temperature coefficient also becomes more negative. These magnetic field effects are also mostly not reversible.

Anomalies of dilatation and elasticity are also known with antiferromagnetic materials. In a manner formally analogous to that of the ferromagnetic materials, an additional dilatation occurs because of antiferromagnetostriction, and thus aΔE-effect. The effect can extend up to the Néel-temperature, which is a corresponding quantity to the Curie-temperature of the ferromagnetic materials, above which, on the transition to a paramagnetic state, there is again a normal behavior of the elasticity. Also, in using terms of the ferromagnetic materials, the origin of the striction resides in a crystal energy, although here with oppositely directed coupled spins.

The effect on the elasticity has been established for the oxides of nickel and cobalt (R. Street and B. Lewis, Nature (London) Vol. 168, p. 1,036, 1951) and a shape antiferromagnetostriction is apparently responsible for a distortion of the lattice from cubic to tetragonal structure. Among the metals, chromium exhibits a narrowly defined anomaly of elasticity at the Néel-temperature and high manganese Mn-Cu alloys (R. Street and J.H. Smith, Le Journal de Physique et le Radium Vol. 20, p. 82, 1959) also exhibit an anomaly. However in such systems the phase transformation accompanying antiferromagnetism masks the immediate effect of the antiferromagnetostriction on elasticity and especially is responsible for dimensional instability under thermal cycling which occurs normally in thermocompensating elements.

The properties of the antiferromagnetic materials are unaffected by external magnetic fields, at least up to field strengths which are commonly attained in air-cored coils. With an antiferromagnetic compensating alloy, the disadvantageous shift of the temperature coefficient of elasticity and of the frequency or the dynamic moment in the magnetic field also do not occur.

Such component elements are applicable not only to oscillating elements of many kinds, which need to exhibit a frequency which is independent of temperature effects, but also to statically loaded component elements, whose E-modulus must remain constant even with changing temperature, such as, for example, springs of spring weighing scales, and even also to mechanically heavily loaded component elements which are to be protected against destructive self-resonances, which might be able to appear on a change of E-modulus.

SUMMARY OF THE INVENTION

According to a feature of the invention the disadvantages of prior art mechanical systems of this type are obviated by adapting the member of the system to be held at one location and moved at another location so that a third portion of the system is strained and making at least the third portion from an antiferromagnetic material having a temperature coefficient of elasticity between $10 \cdot 10^{-5}$ and $-10 \cdot 10^{-5}$ per degree C.

According to another feature of the invention the member is an oscillatory member. According to yet another feature of the invention the member forms part of an oscillatory system.

According to still another feature of the invention the member is composed of 20 percent to 29 percent Mn, 2 percent to 9 percent Cr, 0.03 percent to 1 percent C, and the remainder Fe and ordinary impurities below 1 percent.

According to still another feature of the invention

$$\%mn + (0.6 \times \%Cr) - (5.0 \times \%C) = 21 \text{ to } 27.$$

According to still another feature of the invention up to 4 percent of the Cr can be replaced by Ni, Co, V, Mo, W, Si and up to 0.3 percent of C can be replaced by N. The alloy may also include up to 1.5 percent A1 + Be + Ti + Nb.

These and other features of the invention are pointed out in the claims. Many objects and advantages of the invention will become obvious from the following detailed discussion when viewed in light of the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a watch embodying features of the invention.

FIG. 2 is a schematic diagram illustrating a tuning-fork oscillator system embodying features of the invention.

FIG. 3 is a graph illustrating the change in frequency with changes in the temperature of the oscillating member in FIG. 2.

FIG. 4 is a graph illustrating constant temperature coefficients E as function of the percentages of C with respect to percentages of Mn, and

FIG. 5 is a graph illustrating constant temperature coefficients E as a function of the percentages of Cr with respect to percentages of Mn.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the timepiece **10** of FIG. **1**, a balance **12** oscillates rotationally together with a hairspring **14** which is held fixed at a location **15**. An escapement mechanism **16**, responding to the action of the balance wheel turns a set of reduction gears **18** energized by a mainspring not shown. A dial **20** indicates the time by hands which are turned by the reduction gears **18**. The accuracy of the timepiece **10** depends on the consistency with which the hairspring **14** oscillates the balance wheel **12**.

According to one example the hairspring **14** was made from an alloy composed of 24.8 percent Mn, 5.05 percent Cr, 0.38 percent C, with the remainder Fe and ordinary impurities below 1 percent. The metal was melted in an induction furnace under argon, then hot-rolled at temperatures of 900°C -1,000° C, annealed at 1,000° C and quenched in water. Further transformations were done by cold-drawing and cold-rolling, with intermediate anneals at 900°C to 1,000° C because the metal showed a strong work-hardening. Strips for cutting of tuning forks and fine flattened wire for spiral-hairsprings were obtained.

The behavior regarding temperature behavior and magnetic field effects was tested on a wrist-watch as shown in FIG. **1**. The latter is of ordinary quality (so-called standard caliper produced in large quantities); the equipment of the movement was in particular given by an escapement mechanism made of nickel-silver (except axles), balance wheel **12** made of Copper-Beryllium and the balance staff of steel. It was measured for the temperature coefficient and magnetic influences according to a standard (normes de l'industrie horlogere Suisse). Results are shown in the table, compared to a ferromagnetic spiral-hairspring made of Nivarox 2nd quality.

spiral hairspring made of	temperature coefficient between 4° and 36°C	residual effect after exposure to 60 oersted	watch stops in a field of
Nivarox	+1 sec/day °C	−10 sec/day	150 oersted
Antiferro-magnetic	−1.2 sec/day °C	0 sec/day	700 oersted

The residual effect is a permanant perturbation.

The same metal was used for making a tuning fork **22** for a tuning fork oscillator **24** shown in FIG. **2**. The tuning fork **22** was 3 cm long and 3 mm thick. The oscillation was maintained by an amplifier coupled to the tuning fork **22** by electrostatic transducers **28** and **30**. The frequency variation of the oscillator **24** with temperature is shown in FIG. **3**. The oscillator proved to be sensibly temperature-independent from −20 to +80° C. Above the latter temperature the ΔE-effectanomaly near the Néel-temperature is clearly noticeable. The frequency changed less than 10^{-5} in a field up to 1,000 oersted. The same tuning fork made of the thermocompensating metal Nivarox-Thermelast showed a similar temperature behavior but frequency shifted by about 5 Hz in a magnetic field of 200 Oersted and a residual effect, after exposure to this field, was 0.4 Hz.

In studies of a large number of alloys, melted and transformed to bars, then measured in flexure vibrations, it was found:

higher Mn content increases Néel-Temperature but temperature coefficient becomes negative.

Carbon increases temperature coefficient but leaves Néel-Temperature unaffected.

Chromium decreases Néel-Temperature and temperature coefficient goes negative.

Co, Ni, V, Mo, Si decrease Néel-Temperature and temperature coefficient of elasticity goes negative; up to 4 percent of these elements the laws correspond sensibly to the influence of Cr.

Be, Ti, Al, Nb, which are additives for precipitation hardening, behave similar to Cr.

N acts like C.

These results are graphically and numerically given in FIGS. **4** and **5**, where constant temperature coefficients are shown as functions of carbon and chromium, respectively. The variation of this temperature coefficient of elasticity with Mn can be read on the Mn-line. A general relation for these influences has now been found; if the temperature coefficient of elasticity has to lie between $-10 \cdot 10^{-5}$ and $+10 \cdot 10^{-5}$ per degree it must be

$$\%Mn + (0.6 \times \%\ Cr) - (5.0 \times \%\ C) = 21 \text{ to } 27$$

This is in fact a relation between the special antiferromagnetic phenomena which are on the origin of the elasticity behavior. In this relation *Cr* and *C* can be substituted to a certain extent by the above named metals and this allows to influence workability (example 4 percent Ni) or corrosion resistance (Example 1 percent Mo) or strength.

The additions of Al, Be, Ti, Zr, Nb, Ta and Cu produce precipitation hardening more easily, while the additions of C and N tend also to stabilize the austenitic modification and additionally produce a greater stability on cold working.

The following table shows other examples of the composition used in the hairsprings **16** and tuning forks **22.** They exhibit a temperature coefficient of elasticity about zero near room temperature. Each of the materials in these examples was manufactured in the manner corresponding to the first example above.

1)	24.8% Mn	5.1% Cr	0.47% C	remainder Fe
2)	20.0% Mn	5.4% Cr	0.03% C	remainder Fe
3)	28.2% Mn	2.0% Cr	1.0% C	remainder Fe
4)	23.0% Mn	8 % Cr	0.6 % C	remainder Fe
5)	25 % Mn	5 % Cr	0.4 % Al	remainder Fe
6)	23.0% Mn	6 % Cr	2% Mo 0.6%C	remainder Fe high hardness
7)	25 % Mn	3 % Cr	2% Ni 0.39C	remainder Fe good workability

The following are other examples of the composition of the hairspring **16** and the tuning fork **22.** They exhibit temperature coefficient of elasticity about $+5 \cdot 10^{-5}$ per degree near room temperature.

8)	23% Mn	3 % Cr	0.5% C		remainder Fe
9)	23% Mn	2 % Cr	1 % Co	0.5% C	remainder Fe
10)	23% Mn	2 % Cr	0.5% Be	0.03%C	remainder Fe
11)	24% Mn	1.2% Ti	2.0% Cr	0.03%C	remainder Fe

The thermoelastic coefficients of the aforementioned alloys and further alloys lying in the given range may be adjusted to the desired values in the desired temperature range, for example in the particularly interesting range between −30 and +60° C, by a corresponding heat treatment and an appropriate hot or cold working. A spiral hairspring of alloy 1) affords good thermocompensation when cold worked for about 70 percent before coiling and then subjecting it to a setting heat treatment at 580° C for 1 hour. The temperature coefficient shifts to about $2 \cdot 10^{-5}$ per degree when setting is done at 630° C. The variation with cold work and/or final heat treatment lies however inside the range of $10 \cdot 10^{116\ 5}$ per degree.

For alloys comprising the precipitation agents Al, Be, Ti, Nb, the solution anneal is done at a temperature higher than 850° C and the final heat treatment (precipitation) in the range of 400°C to 750° C.

With reference again to FIG. **1**, the forces which are applied to the spring arise originally, in the conventional manner, from the mainspring, not shown, in the escapement mechanism **16.** The latter intermittently applies forces through the balance **24** to the portion of the spring, namely the end E connected to the balance. The spring has a reaction force applied thereto at another portion, namely the other end *e* at location **15** where it is restrained. The portion between the end, namely the large portion of the spring is intermittently stressed to cause oscillation. These oscillations then actuate the escapement mechanism **16** which turns the reduction gears **18** and the hands on the dial **20.**

Similarly, the tuning fork **22** is composed of three portions. One of these, the lower end, is restrained. The second of these has a vibratory force applied thereto by the electrostatic transducer **28.** The last of these, the intermediate portion, is intermittently and elastically strained. The vibration of the fork actuates the electrostatic transducer **30.** The latter translates the vibration into electrical oscillation which the amplifier applies to the tuning fork actuating electrostatic transducer **28.**

While embodiments of the invention have been described in detail, it will be obvious to those skilled in the art that the invention may be embodied otherwise without departing from its spirit and scope.

What is claimed is:

1. an elastic mechanical system comprising a first portion, a second portion, and a third portion joining said first and second portions, said first portion being adapted to have a force applied thereto, said second portion being adapted to have a reactive force applied thereto so as to strain said third portion, said third portion being composed of an antiferromagnetic material having a modulus of elasticity with a temperature coefficient between $-10 \cdot 10^{-5}$ and $10 \cdot 10^{116\ 5}$ per degree Centigrade.

2. A system as claimed in claim **1**, wherein said third portion comprises 20 to 29 percent Mn, 2 to 9 percent *X*, 0.03 to 1 percent *Y*, 0 to 1.5 percent Al, Be, Ti, Nb, with the remainder Fe and impurities below 1 percent, wherein *X* is Cr + Ni + Co + V + Mo + W + Si but Ni + Co + V + Ro + W + Si only from 0 to 4 percent, and wherein *Y* is C + N but N only from 0 to 0.3 percent.

3. A system as claimed in claim **2**, wherein the weight percentages $\%Mn + (0.6 \times \%\ X) - (5.0 \times \%\ Y) = 21$ to 27.

4. A system as claimed in claim **2**, wherein the weight percentages $\%\ Mn + (0.6 \times \%\ Cr) - (5.0 \times \%C) = 21$ to 27.

5. A system as claimed in claim **4**, wherein said third portion comprises essentially 24.8 percent Mn, 5.05 percent Cr, 0.038 percent C and the remainder Fe and impurities less than 1 percent.

6. A system as claimed in claim **4**, wherein said third portion comprises essentially 24.8 percent Mn, 5.1 percent Cr, 0.47 percent C with the remainder Fe and less than 1 percent impurities.

7. A system as claimed in claim **4**, wherein said third portion comprises essentially 20.0 percent Mn, 5.4 percent Cr, 0.03 percent C with the remainder Fe and less than 1 percent impurities.

8. A system as claimed in claim **4**, wherein said third portion comprises essentially 23.0 percent Mn, 8.0 percent Cr, 0.6 percent C with the remainder Fe and less than 1 percent impurities.

9. A system as claimed in claim **2**, wherein said third portion comprises essentially 25.0 percent Mn, 5.0 percent Cr, 0.4 percent Al with the remainder Fe and less than 1 percent impurities.

10. A system as claimed in claim **2**, wherein said third portion comprises essentially 23.0 percent Mn, 6 percent Cr, 2.0 percent Mo, 0.6 percent C with the remainder Fe and less than 1 percent impurities.

11. A system as claimed in claim **2**, wherein said third portion comprises essentially 25.0 percent Mn, 3.0 percent Cr, 2.0 percent Ni, 0.3 percent C with the remainder Fe and less than 1 percent impurities.

12. A system as claimed in claim **2**, wherein said third portion comprises essentially 23.0 percent Mn, 3.0 percent Cr, 0.5 percent C with the remainder Fe and less than 1 impurities.

13. A system as claimed in claim **2**, wherein said third portion comprises essentially 23.0 percent Mn, 2.0 percent Cr, 1.0 percent Co, 0.5 percent C with the remainder Fe and less than 1 percent impurities.

14. A system as claimed in claim **3**, wherein said third portion comprises essentially 23.0 percent Mn, 2.0 percent Cr, 0.03 percent C 0.5 percent Be with the remainder Fe and less than 1 percent impurities.

15. A system as claimed in claim **3**, wherein said third portion comprises essentially 26.0 percent Mn, 2.0 percent Cr 1.2 percent Ti, 0.03 percent C with the remainder Fe and less than 1 percent impurities.

16. An elastic mechanical system comprising an elastic member, actuating means for straining and and releasing said member, said member being composed of an antiferromagnetic material having a modulus of elasticity with a temperature coefficient between $-10 \cdot 10^{116\ 5}$ and $10 \cdot 10^{116\ 5}$ per degree Centigrade.

17. An elastic system as claimed in claim **16** wherein said member comprises 20 to 29 percent Mn, 2 to 9 percent *X*, 0.3 percent to 1.0 percent *Y*, 0 to 1.5 percent Al + Be + Ti **30** Nb with the remainder Fe and impurities below 1 percent, wherein X is Cr + Ni + Co + V **30** Mo + W + Si but Ni + Co + V + Mo + W + Si only from 0 to 4 percent and wherein Y is C + N but N only from 0 to 0.3 percent.

18. A system as claimed in claim **17**, wherein % Mn + (0.6 × % X) − (5.0 − %Y) = 21 to 27.

19. A system as claimed in claim **17**, wherein % Mn + (0.6 × % Cr − (5.0 × % C) = 21 to 27.

20. A system as claimed in claim **17**, wherein said actuating means vibrate said member so as to form an oscillatory system.

21. A system as claimed in claim **20**, wherein said member comprises 20 to 29 percent Mn, 2 to 9 percent *X*, 0.3 to 1 percent *Y*, 0 to 1.5 percent Al + Be + Ti + Nb with the remainder Fe and impurities below 1 percent, wherein X is Cr + Ni + Co + V + Mo + W + Si but Ni + Co + V + Mo + W + Si only from 0 to 4 percent, and wherein Y is C + N but N only from 0 to 0.3 percent.

22. A system as claimed in claim **21**, wherein % Mn + (0.6 × % *X*) − (5.0 × % *Y*) = 21 to 27.

23. A system as claimed in claim **21**, wherein % Mn + 0.6 *X* %Cr − 5.0*X*%C = 21 to 27.

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