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Steinemann et al.

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[54] **CONSTRUCTION ELEMENT HAVING STRONGLY NEGATIVE TEMPERATURE COEFFICIENTS OF ELASTICITY MODULI**

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[21] Appl. No.: **84,307**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 663,748, Aug. 28, 1967, abandoned, Continuation-in-part of Ser. No. 631,686, April 18, 1967, Pat. No. 3,547,713.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**.................... **148/32.5**, 75/67, 75/134 A, 75/152, 75/177, 148/27, 148/121, 148/158

[51] **Int. Cl.** **C22c 33/00**, H011 3/00, C22b 29/00

[58] **Field of Search**...................... 148/32, 32.5, 158, 148/161, 27, 13; 75/175.5, 177, 152, 134 R, 134 N, 134 A, 67; 84/409, 405, 410, 457

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[57] **ABSTRACT**

The disclosure is directed to construction elements having highly negative temperature coefficients of the moduli of elasticity, and which are characterized in that the construction elements consists of, or contain as the predominant phase, a metal having a paramagnetic atomic susceptibility $x \geqq 40, 10^{-6}$ emu/g-atom at room temperature, and also a positive temperature coefficient of this susceptibility $1/x\ dx/dT$. Furthermore, the construction element is characterized by a preferred orientation of the crystallites of the metal and which preferred orientation has a rigid orientation relationship to the occurring mechanical load.

The materials of the construction elements may be, for example, alloys of Sr and Ca, Ti and Al, Zr and Sc, and multicomponent alloys as Ti-Zr-Al, Ti-Sc-Al. The elements may consist of a samarium-base alloy. The construction elements also may be characterized in that the metal contains limited amounts of B, C, N or O, so-called interstitials of low atomic size.

The disclosure is also directed to methods of producing the preferred orientations by cold-working, annealing, or both and these processes are also applicable for hardening the metal by dispersion or precipitation.

A specific example of an article in the disclosure is a tuning fork useable as a temperature sensor by virtue of its marked change in resonance frequency with changes of temperature.

7 Claims, 5 Drawing Figures

2 Sheets-Sheet 1

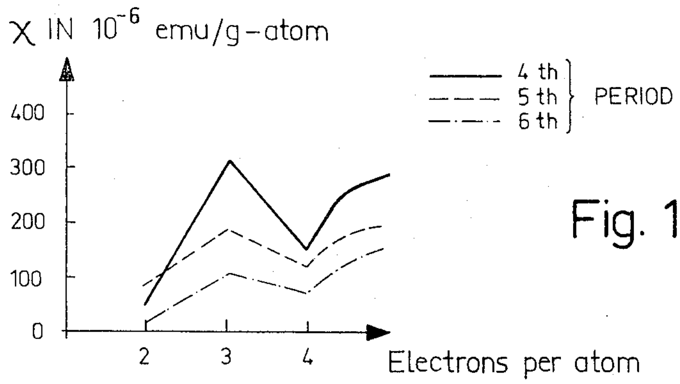

Fig. 1a

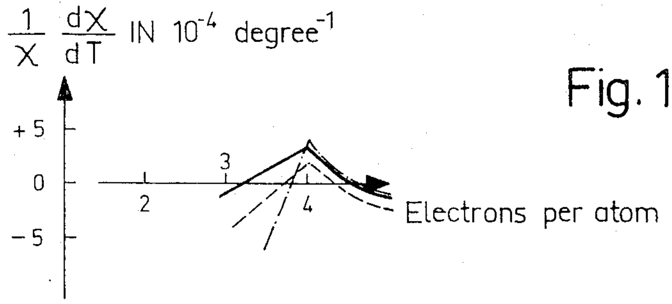

Fig. 1b

Fig. 1c

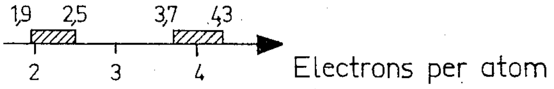

Fig. 2

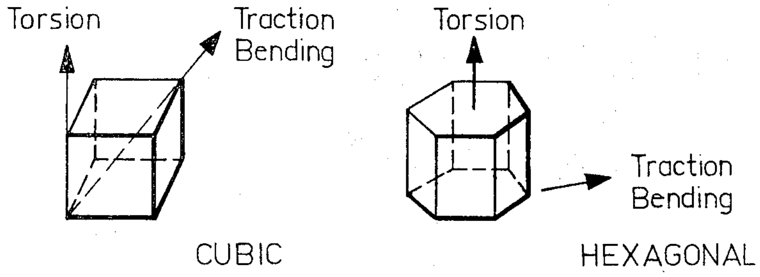

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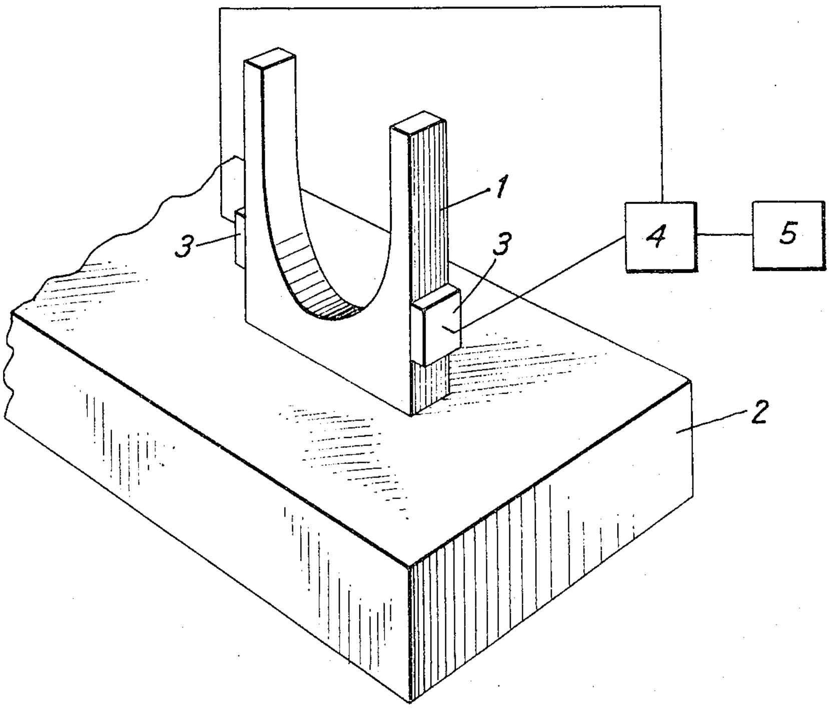
FIG. 3



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CONSTRUCTION ELEMENT HAVING STRONGLY NEGATIVE TEMPERATURE COEFFICIENTS OF ELASTICITY MODULI

CROSS REFERENCE TO PRIOR APPLICATION

This is a continuation-in-part of application Ser. No. 663,748, filed on Aug. 28, 1967, now abandoned, and of application Ser. No. 631,686 of Apr. 18, 1967, now U.S. Pat. No. 3,547,713.

BACKGROUND OF THE INVENTION

Normally no particular requirements are imposed on the temperature behavior of constructional parts in respect of dilatation or elastic properties. There are, however, cases where the dilatation of a material should remain constant or small with varying temperature (gauges, standard measures, pendulum, glass-metal connections, etc.) or where the dependence on temperature of the elasticity of the material or of the articles produced therefrom is prescribed, as, for example, for spiral springs in clocks and measuring systems, for tuning forks, for electromechanical oscillators, and so on. In such cases the temperature coefficients of elasticity are always specified as normal (that is to say of the order of magnitude $e = 1/E\ dE/dT =$ minus $1 \cdot 10^{-4}$ to $3 \cdot 10^{-4}$ per degree) or low (that is to say between plus $1 \cdot 10^{-4}$ degrees^{-1} and minus $1 \cdot 10^{-4}$ degrees^{-1}). These special materials come in the class of the invars, elinvars, etc., and the effect utilized is based on ferromagnetic phenomena which can provide the desired behaviour for dilatation and elasticity within limited temperature ranges.

The converse of these requirements, namely a high dependence of elasticity on temperature, can have important application in technology, and these may be of two kinds. Such a structural material can, for example, serve as a thermometer if the propagation of sound or a vibration frequency is measured in a body made of this material. On the other hand, the requirement of high dependence of the elasticity on temperature may also exist for component parts if, for example, it is desired to obtain less stiffness or to suppress high resonance frequencies with rising temperature for rotating components or components which are liable to resonate (for example for turbines,rockets, instrument suspensions etc.). Still other applications will come for materials with such particular elastic properties, hithertoo not available.

There are some pure metals having low melting points, such as cadmium, tin, and indium, which have highly negative temperature coefficients. But their low hardness and the low melting point make them unsuitable for the purposes mentioned.

There is, however, a group of materials having good mechanical properties, insensitivity to magnetic fields, high melting temperatures, resistance to corrosion, good processability and so on, which also have the desired high dependence of elasticity on temperature over a large temperature range. This dependence on temperature takes a negative course, that is to say the moduli of elasticity (modulus of shear G, modulus of elasticity E) decline with rising temperature.

SUMMARY OF THE INVENTION

Various contributions make up the cohesion energy of a metal. Elasticity is a cohesive property. There are essentially three contributions to this energy to be considered which are caused by the reciprocal action respectively between the ions of the crystal lattice, between ions and free electrons, and between the free electrons themselves. The first two contributions mentioned give determined uniform features of the elastic behavior of the crystal. The last-mentioned contribution, which can be termed the electron gas contribution, governs on the other hand the temperature behavior of elasticity of certain metals and alloys. The large temperature dependence of the elasticity of the metals of this invention is based on such effects.

The present invention is related to metallic construction elements having highly negative temperature coefficients of the moduli of elasticity, and characterized in that they consist of, or contain as a predominant phase, a metal which has at room temperature a paramagnetic atomic susceptibility X larger than $40 \cdot 10^{-6}$ emu/g-atom, and also a positive temperature coefficient of the susceptibility $1/X\ dX/dT$. As is seen, the selection of these metals is based on new selection principles which can be explained by electron theory. In fact, the conditions for the susceptibility stress in an unique way the condition, that the electron gas makes a contribution to elasticity.

The contribution of the electron gas to elasticity is given by the kinetic energy of this electron gas. A direct measure of this energy is the specific heat at low temperature (also called electron heat) and, like the susceptibility, it measures the density of states. The susceptibility figure of $40 \cdot 10^{-6}$ emu/g-atom corresponds to about a specific heat coefficient of $8 \cdot 10^{-4}$ cal/g-atom degree. A high susceptibility, or what is equal, a high density of state and high energy of the electron gas will correlate to the distortion of the crystal lattice, that is to elasticity. It has been found by experiment that the especially interesting temperature behaviour is correlated to the temperature variation of the susceptibility by the unique rule: the temperature coefficient of the susceptibility $1/X\ dX/dT$ must be positive for a strong negative temperature coefficient of elasticity, e.g., $1/E\ dE/dT$ or $1/G\ dG/dT$; this rule applies if X is sufficiently large.

A second basic element of this invention is preferred orientation. The strong negative temperature coefficient of the metal is a single crystal property and anisotropic. It has been found that the strong temperature dependence of elasticity occurs only for certain directions, that is, it is anisotropic, The engineering metals however are polycrystalline and therefore, provisions must be made to produce a minimum amount of preferred orientation of all crystallites and furthermore the load axis of the construction element must be specified relative to this preferred orientation. These conditions then say that the anisotropic crystallites are all oriented in such a way to give the strong temperature dependence of elasticity.

Another object of the invention is to provide metallic construction elements having strong negative temperature coefficients of elasticity and which are of high mechanical strength.

BRIEF DESCRIPTION OF THE DRAWINGS

For an understanding of the principles of the invention, reference is made to the following description of typical embodiments thereof as illustrated in the accompanying drawings.

In the drawings:

FIG. 1*a* graphically represents the paramagnetic susceptibility X;

FIG. 1*b* graphically represents the temperature coefficient $1/x \cdot dx/dT$ of the paramagnetic susceptibility as a function of the electron per atom ration e/a for the transition elements of the 4th, 5th and 6th period of the periodic table and their alloys;

FIG. 1*c* the preferred electron per atom ratios for the metals for construction element; and

FIG. 2 shows a cubic and hexagonal cell of a crystal lattice with the orientation of the loud axis of the construction element giving the highest negative temperature coefficient of elasticity; and

FIG. 3 is a schematic perspective view of a measuring device embodying the invention.

The values for the graphical illustration in FIGS. 1*a*, 1*b* and 1*c* have been collated from many literature sources, and own data.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Metals utilizable for the construction elements according to the invention must be paramagnetic and have a high magnetic susceptibility x and a positive temperaturecoefficient $1/x\ dx/dT$ of this susceptibility.

As can further be seen from FIGS. 1*a* and 1*b*, the following electron per atom ratios inscribe utilizable paramagnetic metals: 1.9 to 2.5 and 3.7 to 4.3.

The electron per atom ratio e/a completely circumscribes all alloys having two or more components between te elements of different groups and periods of the periodic system. The electron per atom ratio is the mean number of electrons to be counted beyond closed shells. This is the number of electrons which are decisive for bonding, to the number of atoms. In the case of an alloy composed of n elements having the atomic percentages C_i and the number V_i of electrons excluding closed shells (valences) the atomic percentages are therefore calculated as the sum of the products atomic concentration times outer electrons (or valency or group number in the periodic table):

$$\frac{e}{a}=\frac{1}{100}\sum_{i=1}^{h} V_iC_i$$

It has further been found that samarium of the rase earth metals and its alloys has the required conditions of susceptibility.

In the materials for producing the elements of the invention, the strong negative dependence of the moduli of elasticity on temperature extends over wide temperature ranges. This is quite different from the elastic behavior displayed over a narrow temperature range which is due to an anomaly in the traditional sense. Such anomalies occur, for example, with martensitic transformations, order processes, transformations of ferromagnetism into paramagnetism, etc. For a Ti-Al alloy according to the present invention as an example, the strong negative temperature variation is usable from -200° C up to +600° C or even up to the melting point and the change is practically linear. The strong negative temperature coefficients of elasticity of the new materials being a single crystal property, the anisotropy must be taken into account or even be used for the technical employment of the materials. The anisotropy is always transmitted to the polycrystal when preferred orientations are present (see for example G. Wassermann and Johanna Grewen: "Texturen metallischer Werkstoffe" Springer Verlag Berlin — Gottingen — Heidelberg 1962 or C.S. Barret: "Structure of Metals," chapter XIX, McGraw Hill 1952). Less investigation has been made into the manner in which the temperature coefficients of a polycrystalline body depend on preferred orientation. A simple manner of describing such orientation influences consists in determining the direction of load or measurement (in which one of the moduli of elasticity indicated is to act) towards the reference axes of the crystallites, as a mean value.

Referring to Barrett (loc. cit.), the elasticity behaviour of the single cristal is determined by the single crystal moduli and an orientation function Φ; Φ defines the orientation of the load or external stress relative to the axis of the crystal lattices. It is now a standard laboratory technique to determine the mean Φ of a polycrystalline metal relative to some fixed direction or plane of the metallic body or half product (bar, sheet etc.); in this case this fixed direction is the load axis of the construction element. Some special values of the orientation function Φ are:

a. cubic lattice case
load axis parallel to $<100>$ of crystal, $\Phi = 0$
load axis parallel to $<110>$ of crystal, $\Phi = 1/4$
load axis parallel to $<111>$ of crystal, $\Phi = 1/3$
isotropic orientation of crystallites $\Phi = 1/5$
b. hexagonal lattice case
load axis parallel to c-axis $\Phi = 1$
load axis perpendicular to c-axis $\Phi = 0$
isotropic orientation of crystallites $\Phi = 1/4$

The X-ray examination for preferred orientation will give these mean Φ values for polycrystalline metals.

It has been found that, because of the anisotropy of elasticity behavior, it must be:

a. cubic lattice case
load is traction or bending $\Phi > 1/5$
load is torsion $\Phi < 1/5$
b. hexagonal lattice case
load is traction or bending $\Phi < 1/4$
load is torsion $\Phi > 1/4$

The important example to discuss in relation to these prescriptions is the tuning fork of FIG. 3 as a temperature sensor. The tuning fork is made of Ti-4 percent Al alloy which has hexagonal structure. The melted alloy is hot-rolled to form of a bar, then hot-rolled to strip, this strip is annealed at 750° C and slightly cold-rolled.

The preferred orientation in this shape is described by $\Phi \approx 0,2$ relative to the length direction. The tuning fork, whose movement of the prongs gives bending stresses, is cut lengthwise (if transverse Φ would be about 0,4 and not favorable for the strong temperature dependence of resonance frequency). THis manufacturing includes therefore the steps: produce preferred orientation by working and choose the good orientation for the construction element. Another way is to fix the orientation of the construction element in a semiproduct and apply transformation steps for this semiproduct that give the preferred orientation.

A procedure for imparting the material with the preferred orientation is described in detail in our application Ser. No. 631,686, now U.S. Pat. No. 3,547,713.

Preferred orientations for polycrystalline metals are produced by drawing and/or rolling (hot-rolling or cold-rolling) and/or annealing.

Since the present invention requires definite preferred orientation conditions, the manner in which these conditions are satisfied is not of primary importance.

The materials and separable phases of which the articles according to the invention consist, and which have a strongly negative thermoelastic coefficient, depend accordingly on the conditions x large (namely $\geqq 40 \cdot 10^{-6}$ emu/g-atom at room temperature) and dX/dT positive. Their occurrence is not tied to a fixed structure. For $e/a = 1.9$ to 2.5 (about group 2*a* of the periodic system) the close packed cubic structures are predominant, for $e/a = 3.7$ to 4.3 predominantly the hexagonal structure exists.

The moduli of elasticity are rather different for the two ranges of electron per atom ratios and thus permit a selection in this respect also; in fact, different rigidities can be required for a construction element.

The conditions for magnetic susceptibility and electron per atom ratio can be satisfied for alloys comprising transition elements or non-transition elements. Examples of the metals are given in the following table.

No.	Composition			$\frac{e}{a}$ (a)	E 10^3kg./mm.^{2} (b)	χ $10^{-6}\frac{emu}{g\text{-}at}$ (c)	$\frac{1}{\chi}\cdot\frac{d\chi}{dT}$ 10^{-4} degree^{-1} (d)	$\frac{1}{E}\cdot\frac{dE}{dT}$ 10^{-4} degree^{-1} (e)	Structure and remarks
	Elements	Wt. percent	At percent						
1	Sr Ca	95.2 4.8	90 10	2.0	ca. 1,500	ca. 60	Positive	ca. −4	Cubic.
2	Ti Al	90 10	83 17	2.83	10,000	ca. 140	ca. +2.7	ca. −5	Up to about 1,100° C. hexagonal: over about 1,100° C. cubic body-centred.
3	Zr Y	95 5	95 5	3.95	11,000	ca. 140	ca. +2.5	−6 to −8	Hexagonal up to about 800° C.
4	Ti Cu	98.9 1.1	98.5 1.5	4.11	10,000	ca. 150	ca. +3.0	ca. −6	Hexagonal under 900° C.: body-centred cubic above 900° C.: precipitation hardening by quenching from about 800° C. and ageing at 500–600° C.
5	Ti O+N	99.9 0.1	99.6 0.4	3.99	10,000	ca. 160	ca. +3.5	ca. −7	Hexagonal up to about 900° C., cubic above.
6	Ti Al	96 4	93 7	3.93	10,000	ca. 150	ca. +3.5	ca. −6	Hexagonal.
7	Zr Sc	95 5	97.5 2.5	3.97	10,000	ca. 140	--------------	ca. −7	Do.
8	Ti Sn	91 9	96 4	4.0	10,000	ca. 140	ca. +3.0	ca. −6	Do.
9	Ca Al	97 3	98 2	2.02	ca. 2,000	ca. 50	ca. +1.0	ca. −4	Cubic.
10	Ti Zr Al	90 8 2	95 4 1	3.98	10,000	ca. 160	ca. +3.5	ca. −7	Hexagonal.
11	Ti Mo	78 22	87.5 12.5	4.25	10,500	170	ca. +2.0	ca. −3	ω-phase.

[a] Electron per atom ratio.
[b] Modulus of elasticity.
[c] Paramagnetic atomic susceptibility.
[d] Temperature coefficient of susceptibility.
[e] Temperature coefficent of elastic modulus.

For technical alloys which have to comply with the conditions of great strength and hardness and also low mechanical losses, resort is generally had to strengthening procedures, such as cold working, precipitation hardening, multi-phase structure, addition of elements having chemical solution strengthening, and phase transformations, either singly or combined with one another. In the metals for the construction elements according to the present invention, such strengthening procedures are also possible. Example No. 4 is a precipitation-hardening alloy; the metal is quenched from temperatures in the region 800° to 1,100° C and precipitation-annealed at 400° to 600° C and cold-working can be performed between the two operations. Example No. 5 is a dispersion-hardening alloy (alloying elements are B,C,O,N, the so-called interstitials up to 5,000 ppm); operations are nearly the same as for the former alloy.

FIG. 3 of the drawing illustrates an example of construction of an article according to the invention. This is a measuring device **1** in the form of a tuning fork, which may, for example, consist of one of the materials listed in the table and which is here used to measure the temperature of the body **2** or of the ambient. For this purpose the measuring body **1** carries electromechanical transducers **3**, which may, for example, be piezocrystals, which maintain an oscillation through a feedback circuit **4**, the measurement of frequency being effected in the circuit unit **5**.

Since the modulus of elasticity of the body has great dependence on temperature, its natural frequency is also correspondingly dependent on temperature, and the natural frequency measured in the circuit unit **5** serves as a measure of the temperature. Since the accuracy of indication is independent of the properties and of any variations of the transmission members, a very convenient temperature measurement device is thus obtained, which works reliably even at high temperatures, and in which the indication can be made at a point at a great distance from the point of measurement because frequency measurement suffers few perturbation. The variation of frequency of an arrangement of this type amounts to about 0.5 per thousand per degree and is largely constant over a temperature range of several hundred degrees.

This tuning fork can be produced by cutting or stamping it out of a metal sheet which has the properties according to the invention, and thus, for example, consists of alloy No. **4** in the table. The preferred orientation has been produced by hot-rolling and still reinforced by the heat treatment at 800° – 1,100° C and cold-rolling. Cutting of the tuning fork ist now done for the condition $\Phi<0.25$, e.g., in lengthwise direction for a cold-rolled and flattened bar (for other shapes Φ can call for other orientations).

Any other article in which a highly negative temperature coefficient for the whole or part of it is desired or necessary may obviously also be produced from the structural matterial, such as for example parts of machines running at high speed and tending towards undesirable natural vibrations, and wherein the natural frequency of these parts should decrease with rising temperature. The stiffness of such materials decrease with increasing temperature, however, their strength is not markedly affected up to 600° C or even higher. Such conditions for a structural material can also be desirable in aeronautic construction.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles.

What is claimed is:

1. A temperature sensitive metallic construction element comprising an alloy, said alloy consisting essentially of a major portion of strontium and a minor portion of another element selected from Group II*a* of the Periodic Table, and further characterized by having

a. a highly negative temperature coefficient of the moduli of elasticity, a paramagnetic atomic susceptibility $X \geqq 40 \cdot 10^{-6}$ emu/mol and a positive temperature coefficient $1/X\ dX/dT$

b. said element having a prereferred orientation which generates anisotropy of the temperature coefficients of the moduli of elasticity by cold-working or annealing, said preferred orientation being defined by the mean value of the product sum of the direction cosine taken overall the crystalline orientations with respect to the stress direction, said value being greater than 0.2 for the elastic modulus and smaller than 0.2 for the shear modulus.

2. A construction element as claimed in claim **1**, in which said alloy further comprises an amount of the elements H, B, C, N or O, said amount not exceeding 5,000 ppm.

3. A construction element as claimed in claim **1**, wherein said alloy is hardenable by subjecting it to precipitation hardening or dispersion hardening heat-treatment.

4. A construction element as claimed in claim **1**, wherein said alloy consists essentially of 85–99 atomic percent of titanium, the remainder being aluminum.

5. A temperature sensitive metallic construction element comprising an alloy, said alloy consisting essentially of a first element selected from the Group IVb of the Periodic Table and one or more additional elements selected from the transition metal series, tin and aluminum and further characterized by having

a. a highly negative temperature coefficient of the moduli of elasticity, a paramagnetic atomic susceptibility $X \geqq 40 \cdot 10^{-6}$ emu/mol, a positive temperature coefficient $1/X\ dX/dT$, and

b. an electron concentration of between 3.7 to 4.3,

c. said element having a preferred orientation which generates anisotropy of the temperature coefficients of the moduli of elasticity by cold-working or annealing, said preferred orientation being defined by the mean value of the product sum of the direction cosine taken overall the crystalline orientations with respect to the stress direction, said value being smaller than 0.25 for the elastic modulus and greater than 0.25 for the shear modulus.

6. A construction element as claimed in claim **5**, in which said alloy further comprises an amount of the elements H, B, C, N or O, said amount not exceeding 5,000 ppm.

7. A construction element as claimed in claim **5**, wherein said alloy is hardenable by subjecting it to precipitation hardening or dispersion hardening heat-treatment.

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