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(54) NIOBIUM-MOLYBDENUM ALLOY COMPENSATING BALANCE SPRING FOR A WATCH OR CLOCK MOVEMENT

(57) The invention relates to a balance spring for a watch or clock movement made of a niobium-molybdenum alloy of formula

$$(Nb_{1-x}M^1{}_x)_n(Mo_{1-y}M^2{}_y)_mM^3{}_zM^4{}_u$$

wherein
M^1, M^2, M^3 and M^4 are different from one another,
M^1 is Ta, V or both,
M^2 is W,
M^3 is a strengthening alloying element,
M^4 is a hardening alloying element,

$$0.6 < n \leq 0.98,$$

$$0.02 \leq m \leq 0.4,$$

$$0 \leq x < 1,$$

$$0 \leq y < 1,$$

$$0 \leq z + u \leq 0.03.$$

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The invention also relates to a timepiece movement comprising this balance spring and to a process for making this balance spring.

Description

FIELD OF THE INVENTION

[0001] The invention relates to the field of horology and more particularly to a balance spring of a regulating organ, made of a niobium-molybdenum alloy.

BACKGROUND OF THE INVENTION

[0002] Mechanical watch movements include a regulating organ comprising a balance wheel and a balance spring. Since these movements must accurately function between 8 °C and 38 °C as defined by the COSC (Swiss Official Chronometer Testing), they require materials having elastic properties that do not change with temperature or materials that self-compensate any temperature induced change in their dynamic behavior and the ones of the balance wheel. More precisely, the thermal dilatations of the balance wheel and of the spiral are compensated by a thermal increase of spiral Young's modulus as the temperature increases. Actually, most of materials present a Young's modulus that decreases when the temperature increases. Hence, materials of interest for making balance springs are commonly defined as materials having an anomalous thermoelastic behavior.

[0003] For instance, the balance spring may be made of Elinvar material, which has a temperature independent Young's modulus within a certain temperature range. An example of Elinvar material includes an alloy containing 56% of iron, 36% of nickel and 5% of chromium.

[0004] Many alloys have been developed as alternatives to the Elinvar iron alloys. They include temperature dependent materials that are able to compensate for the variation of their Young's modulus, which results from the temperature and, eventually, from the magneto constriction i.e. the ability of a material to change its shape upon exposure to a magnetic field.

[0005] Since magnetic perturbations are everywhere in today's environment, it is desirable to have non-magnetic field sensitive materials. For instance, EP 0 886 195 discloses a balance spring that is insensitive to magnetic fields since it is made of a paramagnetic niobium-zirconium based alloy. However, the properties of this alloy result from specific heat treatments and doping elements such as 500 ppm or more of an oxygen based interstitial agent. Moreover, this kind of alloys exhibits some precipitates that are difficult to control.

[0006] Alternatively, EP 1 422 436 discloses a silicon based balance spring, which is also insensitive to magnetic fields but with a Young's modulus very sensitive to temperature variations. Thermal compensation can be obtained by a silicon core and an external layer made of silicon oxide. However, silicon based balance springs remain fragile and require additional care with respect to their handling and to the assembly of the regulating organ.

[0007] Although many materials satisfy the requirements for making a balance spring, there is still a need for new materials, easier to produce and to implement.

[0008] The present invention relates to an alloy having an anomalous thermal behavior of the Young's modulus. As opposed to some of the prior art alloys, this alloy does not require a method of preparation involving specific heat treatments. It can be made according to conventional metallurgic methods since its anomalous behavior results from the combination of its alloying elements, and eventually from the texture of the grains in the alloy.

SUMMARY OF THE INVENTION

[0009] The present invention relates to a specific niobium-molybdenum (Nb-Mo) based alloy that exhibits an anomalous thermoelastic behavior. As opposed to Nb-Zr alloys, precipitations do not take place within Nb-Mo alloys. Indeed, the Nb-Mo alloys form a solid solution over the whole composition range.

[0010] More specifically, the invention relates to a balance spring for a watch or clock movement made of a niobium-molybdenum alloy of formula (I):

$$(Nb_{1-x}M^1_x)_n(Mo_{1-y}M^2_y)_mM^3_zM^4_u \qquad (I)$$

wherein

M^1, M^2, M^3 and M^4 are different from one another,
M^1 is tantalum (Ta), vanadium (V) or both,
M^2 is tungsten (W),
M^3 is a strengthening alloying element,
M^4 is hardening alloying element,

$$0.6 < n \leq 0.98,$$

$$0.02 \leq m \leq 0.4,$$

$$0 \leq x < 1,$$

$$0 \leq y < 1,$$

$$0 \leq z + u \leq 0.03.$$

[0011] Amounts x, n, y, m, z and u relate to the respective molar amounts of elements Nb, M^1, Mo, M^2, M^3 and M^4 within formula (I). For instance, for every (1-x) moles of niobium, the alloy of formula (I) contains x moles of M^1.

[0012] The thermal coefficient of elasticity (CTE) of this alloy has an anomalous behavior preferably between -10 °C and 40 °C, more preferably between 8 °C and 38 °C. Due to its anomaly, the alloy does not get more and more flexible as the temperature increases.

[0013] On the other hand, pure niobium exhibits an anomalous elastic behavior due to its c_{44} elastic coefficient from about 500 K. Alloying element(s), such as molybdenum, allow(s) shifting this anomaly to lower temperatures. However, pure molybdenum does not exhibit an anomalous thermoelastic behavior.

[0014] Typically, the alloy of formula (I) has an anomalous thermoelastic behavior that is, at least, due to its shear elastic coefficient c_{44} and/or to its shear coefficient constant c'.

[0015] Although not wishing to be bound to any particular theory, it is believed that the anomaly of the elastic behavior of the alloy of formula (I) could be related:

- to a high density of states at the Fermi level, and
- to a decrease in the number of electronic states during a distortion of the primitive cell in the vicinity of the Fermi level.

[0016] These two conditions are met thanks to the presence of niobium whereas, as already mentioned, molybdenum ensures the shift of the anomaly to the temperature range of interest.

[0017] Further alloying elements such as M^1, M^2, M^3 and M^4 are added so as to adjust the properties required for a balance spring e.g. elasticity, deformability or a low coefficient of expansion. They may also affect the thermoelastic anomaly of the alloy.

[0018] The alloy of formula (I) has a coefficient of expansion that is preferably less than 10.10^{-6}/°C enabling the thermo-compensation of a spring balance assembly.

[0019] In formula (I), "n" and "m" correspond to the respective amounts of alloying elements Nb + M^1 and Mo + M^2.

[0020] The n amount of alloying element(s) Nb+M^1 ranges from more than 0.6 to 0.98 or less.

[0021] As already mentioned, M^1 is Ta, V or both. The amount "x" of element M^1 is strictly less than 1, preferably between 0 and 0.5 ($0 \leq x \leq 0.5$), more preferably between 0 and 0.2 ($0 \leq x \leq 0.2$). Larger amounts of M^1 may cause precipitation, hence, strongly affect the thermoelastic behavior and impede deformability. In general, vanadium maintains the thermoelastic anomaly while tantalum reduces it.

[0022] Element M^1 is preferably vanadium.

[0023] The m amount of alloying element(s) Mo+M^2 ranges from between 0.02 and 0.4.

[0024] As already mentioned, the amount "y" of tungsten (M^2 = tungsten) is strictly less than 1. It preferably ranges between 0 and 0.5 ($0 \leq y \leq 0.5$), more preferably between 0 and 0.2 ($0 \leq y \leq 0.2$).

[0025] M^3 is a strengthening alloying element. It improves the mechanical properties of the alloy. It can also ensure the shift of the thermoelastic anomaly of the alloy, typically to lower temperatures i.e. from -10 °C to 40 °C.

[0026] According to a preferred embodiment, M^3 is a metalloid or a metal other than Nb, Ta, V, Mo and W.

[0027] Metals include alkali metals, alkaline earth metals, transition metals, lanthanides and actinides. On the other hand, metalloids include B, Si, Ge, As, Sb, Te and At.

[0028] M^3 is preferably any one of: Be, Al, Si, Ge, Sc, Y, La, Ti, Hf, Cr, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, or a mixture thereof. Here and elsewhere, any one of means "at least one selected from the group comprising...".

[0029] The alloy of formula (I) exhibits ductility properties that are advantageous in the formation of a balance spring. Indeed, many deformation steps are carried out, for instance the reduction of the section of a wire. Accordingly, the alloy comprises Nb, Mo and preferably any one of Zr, Ta, or Ti, which improve the ductility of the alloy.

[0030] Besides Mo, the presence of any one of V, Ta, Pd, Pt, Ti, Rh and Zr can enhance the shift of the anomaly of the elastic behavior to temperatures that preferably range between -10 °C and 40 °C.

[0031] The amount "z" of the M^3 element within formula (I) is preferably between 0 and 0.02 ($0 \leq z \leq 0.02$).

[0032] M^4 is hardening alloying element. M^4 is preferably any one of: O, N, C, B, P, H or a mixture thereof.

[0033] The amount "u" of the M^4 element within formula (I) is preferably between 0 and 0.01 ($0 \leq u \leq 0.01$).

[0034] The niobium-molybdenum alloy of formula (I) may contain either or both of M^3 and M^4. Accordingly, z + u may be strictly greater than 0.

[0035] When z is strictly greater than 0 (i.e. z + u > 0), M^3 is preferably any one of Cu, Ti, Al, Cr, Mn, Si, or a mixture thereof. These alloying elements, as well as W and V, allow refining the microstructure of the alloy.

[0036] When z and u are both strictly greater than 0, M^3 can be any one of Cr, Ni, Mn, Ti, Zr, Hf or a mixture thereof while M^4 can be any one of C, O, B, N or a mixture thereof. The conditions (kinetics and/or temperature) for preparing and transforming the alloy may be adjusted thanks to these alloying elements, as well as Ta, Mo, V and W.

[0037] According to a particular embodiment, preferably when the alloy comprises any one of Cr, Ti, Al, Si, Fe, W, Ni, Mn, V, N or a mixture thereof, the balance spring made of the alloy of formula (I) may also comprise an oxide layer. This oxide layer acts as a passivation layer and therefore protects the balance spring from corrosion for instance.

[0038] The niobium-molybdenum alloy of formula (I) may be zirconium free and/or chromium free.

[0039] It can be free of magnetic elements such as Fe, Co and Ni.

[0040] According to another embodiment, the alloy of formula (I) is preferably insensitive to magnetic fields.

[0041] The metal elements of the alloy may have similar size and same crystal structure in elemental form in order to enhance the probability to form a solid solution and in order to reduce the probability of forming secondary phases. Elements having the same crystal structure, for instance cubic materials, e.g. body-centered cubic materials, include V, Cr, Mn, Fe, Ta, W, and mixtures thereof, preferably any one of V, Cr, Mn, Ta, W and mixtures thereof, and even more preferably any one of V, Cr, Ta, W and mixtures thereof.

[0042] According to another particular embodiment of the invention, x = y = z = 0. In other words, the niobium-molybdenum alloy may be of formula $Nb_nMo_mM^4_u$.

[0043] The invention also relates to a timepiece movement comprising a balance spring made of the niobium-molybdenum alloy of formula (I). For instance, this timepiece movement may be a watch or a clock.

[0044] The invention also relates to a process for preparing a balance spring made of the niobium-molybdenum alloy of formula (I).

[0045] It can be prepared according to any conventional process, for instance according to a process comprising the following steps:

- casting the alloy of formula (I),
- making a bar of alloy,
- forming a wire of alloy from the bar of alloy,
- shaping the wire into a balance spring,
- optionally, heat-treating the balance spring, preferably between 500 and 1500 °C, more preferably between 650 and 880 °C.

[0046] The above steps (bar making, wire forming and shaping...) include cold/semi-hot transformations of the alloy, which generally texture the alloy. As a result, temperature, transformation rates and heat treatments may be chosen and adjusted to favor and/or preserve the degree of texture.

[0047] Texturing the alloy may be useful in order to adjust the anomaly of the alloy when it depends on the c_{44} elastic coefficient. Indeed, since the c_{44} elastic coefficient is anisotropic, a texturing step may allow adjusting the anomaly of the alloy.

[0048] The anomaly of the alloy of formula (I) depends on the c_{44} and/or on the c' elastic coefficients. As opposed to prior art alloys, the anomaly can be adjusted at two different levels since these two elastic coefficients can be independently adjusted thanks to the alloying elements (c_{44} and c' coefficients) and thanks to a texturing step (c_{44}).

[0049] The skilled person in the art will be able to adjust the experimental conditions of the above steps in order to prepare the alloy of formula (I).

[0050] The invention and its advantages will become more apparent to one skilled in the art from the following figures and examples.

FIGURES

[0051]

Figure 1 shows the density of states in the vicinity of the Fermi level for pure niobium, pure molybdenum and for niobium-molybdenum alloys.

Figure 2 shows the calculated absolute variation in the elastic constants c_{44} and c' as a function of temperature considering constant volume of pure niobium, pure molybdenum and niobium-molybdenum alloys.

EXAMPLES

[0052] Niobium-molybdenum alloys have been compared to pure niobium and pure molybdenum using DFT calculations (density functional theory).

[0053] The exemplified alloys according to the invention are $NbMo_{15\%}$ (n = 0.85; m = 0.15); $NbMo_{24\%}$ (n = 0.76; m = 0.24) and $NbMo_{33\%}$ n = 0.67; m = 0.33).

[0054] They have been compared to pure niobium, pure molybdenum and to the following alloys: $NbMo_{41\%}$ (n = 0.59; m = 0.41) and $NbMo_{50\%}$ (n = 0.5; m = 0.5) that fall outside of formula (I).

[0055] Figure 2 shows that the presence of Mo in the Nb-Mo alloys shifts the minimum c_{44} from 500 K to temperatures close to 0 K as compared to pure Nb. Above 15 % and below 41 % in molybdenum, we observe an increase in the temperature behavior of c', which is not the case for elemental Nb and Mo.

[0056] However, when, the amount of Mo is greater than 40% ($NbMo_{41\%}$ and $NbMo_{50\%}$), which is outside the invention, the influence of the electronic structure contribution decreases since the density of states at the Fermi level also decreases (see figures 1 and 2). These materials almost behave like pure molybdenum.

Claims

1. Balance spring for a watch or clock movement made of a niobium-molybdenum alloy of formula (I):

$$(Nb_{1-x}M^1_x)_n(Mo_{1-y}M^2_y)_m M^3_z M^4_u \qquad (I)$$

wherein

M^1, M^2, M^3 and M^4 are different from one another,
M^1 is Ta, V or both,
M^2 is W,
M^3 is a strengthening alloying element,
M^4 is a hardening alloying element,

$$0.6 < n \leq 0.98,$$

$$0.02 \leq m \leq 0.4,$$

$$0 \leq x < 1,$$

$$0 \leq y < 1,$$

$$0 \leq z + u \leq 0.03.$$

2. Balance spring according to claim 1, ***characterized* in that** the alloy of formula (I) has an anomalous thermoelastic behavior due to its shear elastic coefficient c_{44} and/or to its shear coefficient constant c'.

3. Balance spring according to any of claims 1 to 2, ***characterized* in that** M^3 is a metalloid or a metal other than Nb, Ta, V, Mo and W.

4. Balance spring according to any of claims 1 to 3, ***characterized* in that** M^3 is any one of Be, Al, Si, Ge, Sc, Y, La, Ti, Hf, Cr, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, or a mixture thereof.

5. Balance spring according to any of claims 1 to 4, ***characterized* in that** M^4 is any one of O, N, C, B, P, H or a mixture thereof.

6. Balance spring according to any of claims 1 to 4, ***characterized* in that** z is strictly greater than 0, M^3 is any one of Cu, Ti, Al, Cr, Mn, Si, or a mixture thereof.

7. Balance spring according to any of claims 1 to 6, ***characterized* in that** the alloy of formula (I) comprises an oxide layer.

8. Balance spring according to any of claims 1 to 6, ***characterized* in that** the alloy of formula (I) comprises an oxide layer and any one of Cr, Ti, Al, Si, Fe, W, Ni, Mn, V and N.

9. Balance spring according to claim 1, ***characterized* in that** $x = y = z = 0$.

10. Balance spring according to any of claims 1 to 9, ***characterized* in that** the niobium-molybdenum alloy of formula (I) is zirconium free and chromium free.

11. Timepiece movement comprising the balance spring according to any of claims 1 to 10.

12. Process for making the balance spring of any of claims 1 to 10, according to the following steps:

- casting the alloy of formula (I),
- making a bar of alloy,
- forming a wire of alloy from the bar of alloy,
- shaping the wire into a balance spring,
- optionally, heat-treating the balance spring.

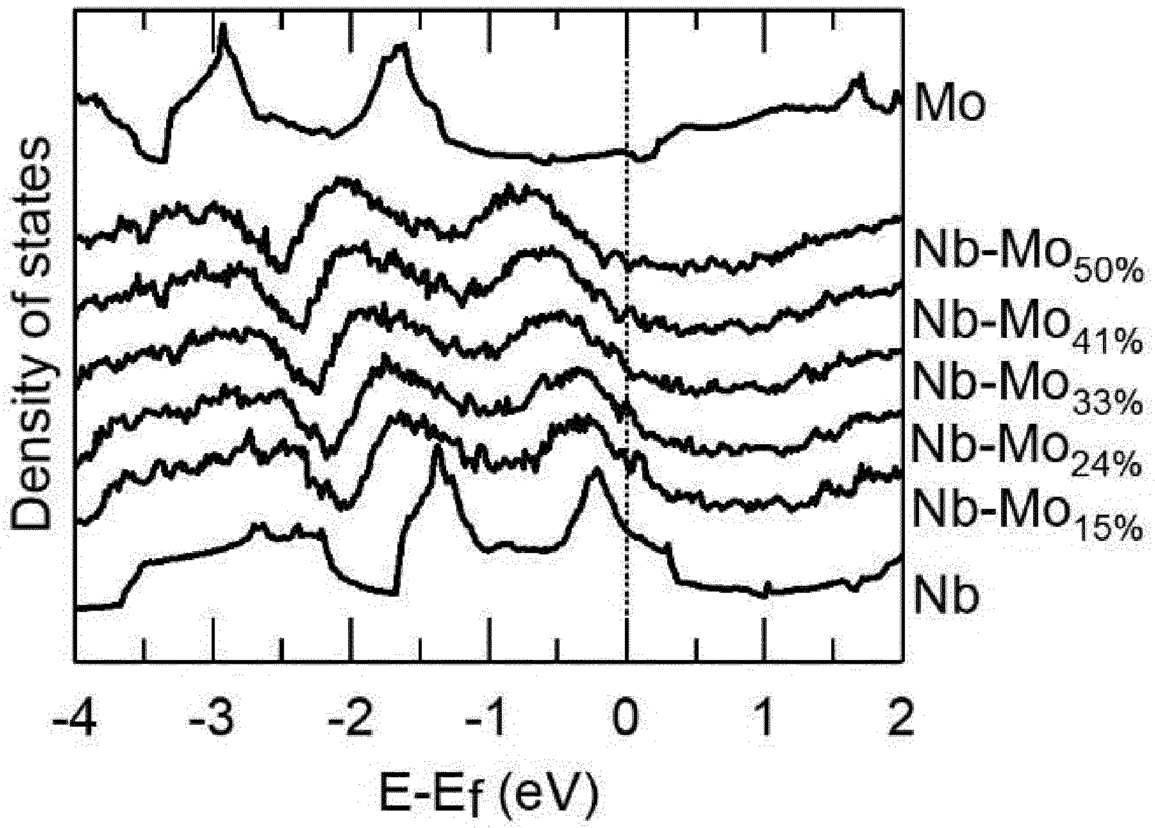
Density of states
Mo
Nb-Mo50%
Nb-Mo41%
Nb-Mo33%
Nb-Mo24%
Nb-Mo15%
Nb
-4
-3
-2
-1
0
1
2
E-Ef (eV)

Fig. 1

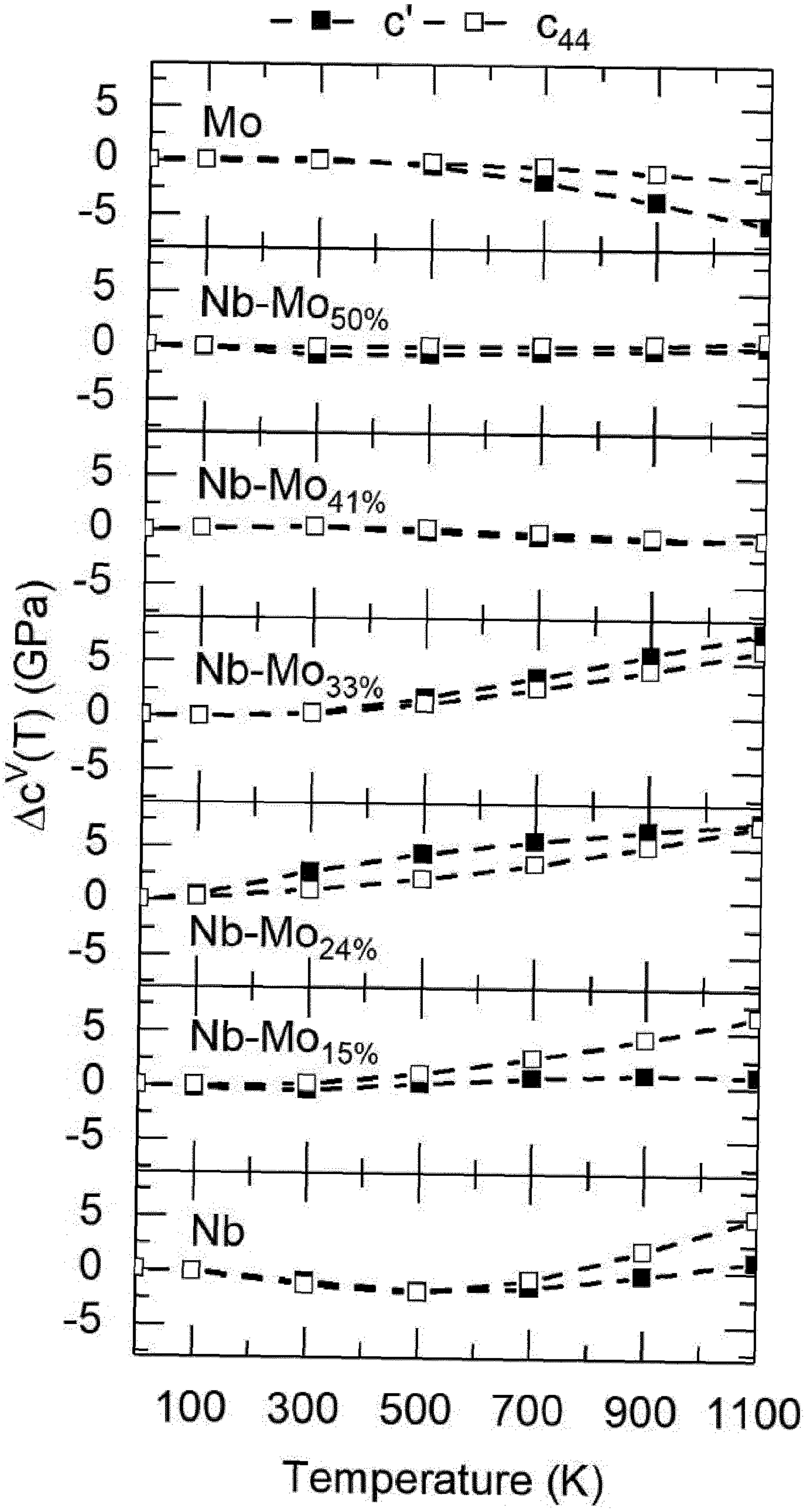
c'
c44
Mo
Nb-Mo50%
Nb-Mo41%
Nb-Mo33%
Nb-Mo24%
Nb-Mo15%
Nb
5
0
-5
ΔcV(T) (GPa)
100
300
500
700
900
1100
Temperature (K)

Fig. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 18 21 0512

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	EP 1 258 786 A1 (ROLEX MONTRES [CH]) 20 November 2002 (2002-11-20) * paragraphs [0015], [0018], [0019], [0020], [0021], [0022]; claims 1,3 *	1-4,7,8, 10-12 5,6,9	INV. G04B17/06 C22C27/02 C22C27/04 C22F1/18
A	US 3 547 713 A (STEINEMANN SAMUEL ET AL) 15 December 1970 (1970-12-15) * column 8, lines 66-71; claim 19 *	1-12	
A	FR 1 521 737 A (STRAUMANN INST AG) 19 April 1968 (1968-04-19) * 5,4% Ti + 10,8% Mo + 83,8% Nb; table I *	1-12	

TECHNICAL FIELDS SEARCHED (IPC)

G04B
C22C
C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	20 May 2019	Cavallin, Alberto

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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20-05-2019

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- EP 1422436 A **[0006]**