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(54) ALLOYS, FOR EXAMPLE, FOR WATCH CASES

(71) We, KABUSHIKI KAISHA SUWA SEIKOSHA, a Japanese company of 5-19, 4-chome, Ginza-Nishi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for

which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an alloy adapted to be used, for instance, in a case for a watch.

The accuracy of a watch is strongly governed by the proper functioning of the hairspring which is usually made of a ferromagnetic thermo-compensating material. Moreover, other elements of the watch influencing its accuracy, such as the escapement wheel, anchor, etc., are also often made of ferromagnetic material such as iron alloy. As a consequence of the fact that the most important parts from the point of view of accuracy of a watch are made of ferromagnetic materials, such a watch will be open to deleterious influences by external magnetic fields. The so-called "anti-magnetic" watches are in general provided with a shield or screen of high permeability material, such as pure iron, permalloy, etc., between the case and the movement to protect the latter from the influences of external magnetic fields. However, such "anti-magnetic" watches, by virtue of having to have a separate magnetic shield, are more complicated in structure, and are more difficult to manufacture and to assembly than ordinary watches. Furthermore, such watches are by necessity heavier in weight and larger in shape than ordinary watches unprotected from external magnetic fields.

The present invention seeks to overcome the above defects.

According to the present invention, there is provided an alloy having the following percentage composition by weight: chromium 16.0-25.0%, molybdenum 1.0-4.0%, carbon less than 0.05%, niobium and/or titanium being present such that when niobium is absent, the titanium content is 3-10 times the carbon content; when titanium is absent, the niobium content is 8-15 times the carbon content; and when both niobium and titanium are present, their combined amount is 5-15 times the amount of carbon; the balance being iron and impurities.

There is also provided a watch case made of the alloy as set forth above.

The invention also includes an anti-magnetic watch having a case as set forth above, but having no additional magnetic shield between the case and the movement thereof.

The invention will be described, merely by way of example, with reference to the accompanying drawing, which is a graph of the variation of the rate of a watch with external magnetic fields, for different materials of watch cases.

Table 1 names and sets out the properties of five materials from which watch cases, especially case bands, dials or back covers have been made, material No. 5 being an alloy in accordance with the present invention.

[*Price 5s. 0d. (25p)*]

TABLE 1

Material	Treatment	Hardness
1. 4-6 brass	30% rolled, gold plated	HV 140
2. 18-8 stainless steel	annealed	175
3. AISI 430 ferritic steel	fully annealed	160
4. pure iron	„ „	70
5. Fe-Cr-Mo-Nb alloy of the present invention	„ „	170

One specific Example of a composition of an alloy in accordance with the present invention is shown below at Table 2; Si and Mn were added as deoxidising agents.

TABLE 2

Cr	Mo	C	Nb	Si	Mn	Fe
19.2	2.0	0.03	0.31	0.6	0.2	balance

Subsequently, experiments were carried out to ascertain the effects of the magnetic field on, and resistance to corrision of, watch cases made from the above materials. The experiments were so performed that the variations of rate were measured by increasing the intensity of magnetic field in which the watches with cases of the above five kinds of materials were placed. The direction of the magnetic field was chosen to be the most unfavourable one, determined from the preliminary experiments to give the greatest disturbance to the rate, i.e. a field located parallel to the plane of the plate of the watch and perpendicular to the escapement line (escapement wheel-anchor balance). The movements in each case were of the same calibre and the torque of the mainspring was arranged to be similar in all the experiments.

The drawing shows the results of the experiments and tests. Most watch cases are made of brass and 18Cr-8Ni austenitic stainless steel cases, and the graph shows that these materials do not have any protective effect against the influences of external magnetism, and even a relatively weak intensity field will influence the rate.

On the other hand, the pure iron case gives a remarkable degree of protection unaffected even in magnetic field intensities of 300 oersteds. In the case of the AISI 430 ferritic steel case (composition: C<0.12%, Mn<1.0%, P<0.04%, S<0.03%, Si<1.0%, Cr 14-18%), the magnetic field begins to influence the rate at about 50 oersteds, while with the alloy of the present invention, the influence begins at about 100 oersteds.

Another experiment was performed to ascertain the residual effects on the watches made with the above described five kinds of materials, by measuring the rates one hour after passing the watches through a magnetic field of 80 oersteds for 1 minute. The results are set out in Table 3.

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TABLE 3

material of case	residual effect
1. Brass	−21 sec/day
2. 18Cr-SNi stainless steel	−20
3. AISI 430 ferritic steel	−3
4. Pure iron	0
5. Fe-Cr-Mo-Nb alloy of the present invention	0

Throughout the experiment, the conditions such as the torque of the mainspring, temperature, and the like were kept constant. As the Table clearly shows, the brass and the 18Cr-8Ni stainless steel cases showed a large residual effect, while the pure iron case and the case made from the alloy of the present invention showed substantially no residual effect at all.

Table 4 shows typical intensities of magnetic fields met in daily use, and from this it will be appreciated that the alloy of the present invention is effective in practice as a magnetic shielding material.

TABLE 4

Origin of magnetic field (Japan)	Intensity in Oersteds
Earth's magnetic field (Japan)	0.5
Telephone receiver	12
Ammeter (Alternative current)	50
Pocket circuit tester	80
Transistor radio	80 to 120
Electric exposure meter	100
Magnetic chuck of surface grinder	100

Next, watches provided with cases made from three of the above described materials were subjected to a one-year wear test. No tests were carried out on a watch case made of pure iron because of its evidently unfavourable corrosion resistance properties, nor was brass tested which is usually gold plated. However, it was observed that the AISI 430 case was extremely corroded, especially at the part where the back cover and the case band meet and this material was therefore ruled out for practical use. On the other hand, neither the Fe-Cr-Mo-Nb alloy case of the present invention or the 18Cr-8Ni stainless steel case were corroded at all.

Moreover, it is found that the Fe-Cr-Mo-Nb alloy has sufficient mechanical strength to serve as a watch case and at the same time was found to have a coercive force as strong as that of pure iron, thereby showing that a watch case made of such an alloy would not be magnetised permanently, when passed through a magnetic field.

Typical maximum permeabilities of the alloy of the present invention are in the range of μ_{max} 2,000 to 6,000, with saturation values of magnetic inductions being in the range of 11,000 to 13,000 gauss, and with coercive forces in the range of 0.1 to 1.0 oersteds.

As far as the corrosion properties are concerned, a comparison was made between the steel of the present invention and the 18Cr-8Ni stainless steel, using a very large number of different corrosion fluids. It was found that the steel of the present invention exhibited at least the same degree of resistance to corrosion as the 18Cr-8Ni stainless steel, and in the case of a 10% solution of

hydrochloric acid, the stainless steel of the present invention was merely discoloured, while the 18Cr-8Ni stainless steel exhibited slight corrosion.

It will be appreciated that a watch provided with a case as described with reference to the accompanying drawing will have its movement protected from external magnetic fields by the case itself and requires no other shielding parts. Consequently, there is no difference in shape, size and structure between the watch of the present invention and an ordinary, not "anti-magnetic" watch, but a saving of weight and complexity is achieved over "anti-magnetic" watches with magnetic shields between their cases and movements.

WHAT WE CLAIM IS:—

1. An alloy having the following percentage composition by weight: chromium 16.0-25.0%, molybdenum 1.0-4.0%, carbon less than 0.05%, niobium and/or titanium being present such that when niobium is absent, the titanium content is 3-10 times the carbon content; when titanium is absent, the niobium content is 8-15 times the carbon content; and when both niobium and titanium are present, their combined amount is 5-15 times the amount of carbon; the balance being iron and impurities.

2. An alloy having the composition as hereinbefore described in the Example at Table 2.

3. An anti-magnetic and corrosion-resistant watch case made of a ferritic stainless steel having the composition claimed in either preceding claim.

4. An anti-magnetic watch having a case as claimed in claim 3 but having no additional magnetic shield between the case and the movement thereof.

5. A case for a watch as claimed in claim 3 substantially as hereinbefore described with reference to the accompanying drawing.

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