United States Patent [19]

Maquelin

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[54] **METHOD FOR THE MANUFACTURE OF AN ELEMENT OF WATCH CASE AND ELEMENT OF WATCH CASE OBTAINED BY THIS METHOD**

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[30] **Foreign Application Priority Data**

Jan. 13, 1971 Switzerland 446/71

[52] **U.S. Cl.** **148/6.3,** 148/6, 148/6.24, 148/13.1, 148/20.3, 148/31.5

[51] **Int. Cl.** **C23c 11/10,** C23c 9/04

[58] **Field of Search** 148/20.3, 6, 6.3, 148/6.24, 13, 31.5, 13.1

[56] **References Cited**

UNITED STATES PATENTS

2,823,151	2/1958	Yntema et al.	148/31.5
2,804,406	8/1957	Yntema et al.	148/31.5
2,665,475	1/1954	Campbell	148/31.5

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[57] **ABSTRACT**

Method of making a watch case element by forming same of molybdenum and hardening by carburization producing a surface layer of molybdenum carbide, said carburization being carried out during the final manufacturing stage. A further treatment of the carburized element with hydrogen sulphide results in the formation of a dark coloured polishable surface which has fine brilliance.

18 Claims, No Drawings

METHOD FOR THE MANUFACTURE OF AN ELEMENT OF WATCH CASE AND ELEMENT OF WATCH CASE OBTAINED BY THIS METHOD

The present invention provides a method for manufacturing an element of a watch case and the element of watch case so obtained.

For the past several years research has been carried out in order that the watch-making industry might have available watch cases presenting a hard surface which would conserve their beauty and brilliance over the longest possible time. Several solutions already have been proposed, among which are the sintering of carbides, the utilization of stainless steel hardened by nitriding and covered by hard chrome, the application of carbides by spattering as well as the utilization of ordinary steel hardened by chemical vapour deposition of carbides.

All of these solutions present certain disadvantages.

Watch cases resulting from sintering are strictly limited in their forms and moreover, are very fragile.

A watch case in stainless steel hardened by nitriding requires, in order to obtain a sufficient corrosion resistance, to be further protected by stainless steel hardened through a layer of chrome such processes imply numerous difficulties.

The application of carbide by spattering produces a surface layer much too porous to permit the type of surface which one wishes to obtain through simple polishing.

Finally, the utilization of ordinary steel hardened by chemical vapour deposition of carbides produces a superficial layer of a hardness such that the final polishing thereof is almost impossible.

The present invention proceeds from the idea of machining a watch case from a material capable of being hardened as a last operation. It is understood that this material must be non magnetic, corrosion resistant, particularly in respect of sea water, easily machinable and capable of either hot or cold forming.

The method according to the invention is characterized by the fact that one fashions the element of watch case of molybdenum and that one hardens it during the finishing stage by a carburizing treatment, thereby producing on the surface thereof a layer of molybdenum carbide.

The element of the watch case so obtained is characterized by the fact that it comprises molybdenum having a surface covering of molybdenum carbide.

Molybdenum has shown itself to respond to the requirements mentioned hereinbefore. It is to be noted that the hardening of the watch case element obtained during final stages of manufacture does not comprise a cementation in the usual sense of this term, i.e. comprising a very hard surface zone united to the interior by a transitional zone. Instead a carburization occurs producing molybdenum carbide at the surface.

The hardening operation, by carburization, is effected by burying the otherwise finished items in a cement of the classic type, by welding shut the container in order to assure a complete sealing thereof, and by bringing this cement to and holding it at a temperature from 1100° to 1300°C for a duration of 10 to 15 hours or still longer should one wish to obtain a very deep carburization.

The cooling must be effected in the oven and very slowly in order to prevent the carbide zone from becoming fragile. Once the element has reached the room temperature, one can reheat it at a temperature of about 1000°C during about two hours, letting it then to cool again very slowly. This improves the diffusion of the hardening layer and reduces the fragility of the element.

The hardness thus obtained is of the order of 1500 to 1700 Vickers measured by micro-hardness at a load of 500 g. The depth of carburization is in the order of 10 to 300 microns according to the temperature and the time. There will be no deformation since molybdenum at 1000°C has the same resistance as iron at 20°C. A simple polishing will give the desired brilliance.

The hardening by carburization also can be carried out in a vessel made of a ceramic, the cement of which is constituted by 60 percent of active carbon, 30 percent of graphite and 10 percent of charcoal. The duration of the operation will be of about 20 hours, at a temperature of about 1300°C, for obtaining a hard layer of a thickness of 150 microns. The hardness of such layer is of the order of 1500 to 1600 Vickers at a load of 500 g.

The hardening also can be carried out under a controlled atmosphere containing 98 percent of hydrogenous and 2 percent of methanol.

A dark coloured surface having a very fine brilliance and capable of being polished without difficulty may be obtained by treating the carburized items in an atmosphere of hydrogen sulphide at a temperature of about 850°C during about 20 minutes, thereby forming a compound molbydenum-sulphide on the surface.

Since molybdenum has the property of being easily oxydizable above 500°C, various colours such as blue and organge may be obtained through modifying the chemical composition of the surrounding atmosphere or by means of a galvanic oxydation in baths hardly acid or alkaline, even caustic, i.e. other than neutral.

I claim:

1. Method of manufacturing an element of a watch case, characterized by the fact that the said element is formed of molybdenum and is hardened during the final manufacturing stage by carburization thereby to produce a surface layer of molybdenum carbide.

2. Method according to claim **1,** characterized by the fact that the hardening is carried out in a cement at a temperature of 1100° to 1300°C, for a duration of 10 to 15 hours.

3. Method according to claim **1,** characterized by the fact that the hardening is carried out in a cement constituted by 60 percent of active carbon, 30 percent of graphite and 10 percent of powder of charcoal.

4. Method according to claim **1,** characterized by the fact that the hardening is carried out during about 20 hours, at a temperature of about 1300°C.

5. Method according to claim **1,** characterized by the fact that the hardening is carried out under a controlled atmosphere contained 98 percent of hydrogenous and 2 percent of methanol.

6. Method according to claim **1,** characterized by the fact that once the hardening is effected, the element is reheated at a temperature of about 1000°C, for a duration of about two hours, and then cooled very slowly.

7. Method according to claim **1,** characterized by the fact that the element, after the hardening, is further treated in an atmosphere of hydrogen sulphide in order to form on the surface thereof a compound of molybdenum-sulphide so as to give a darkened colour to the said element.

8. Method according to claim 7, characterized by the fact that the treatment in the hydrogen sulphide atmosphere is carried out at a temperature of approximately 850°C and for a duration of approximately 20 minutes.

9. Method according to claim 1 characterized by the fact that the element is coloured either by changing the composition of the surrounding atmosphere, or by a galvanic treatment in a bath other than neutral.

10. A watch case element formed of molybdenum and having a surface layer of molybdenum carbide formed by hardening during the final manufacturing stage by carburization.

11. A watch case element as claimed in claim 10 in which said molybdenum carbide surface layer has an outer layer formed of a compound of molybdenum-sulfide.

12. A watch case element as claimed in claim 10 in which said molybdenum carbide surface layer has a hardness in the range of the order of 1500 to 1700 Vickers measured by micro-hardness at a load of 500 grams.

13. A watch case element as claimed in claim 10 in which said molybdenum carbide surface layer has a thickness of the order of from 10 to 300 microns.

14. A watch case element as claimed in claim 10 in which said molybdenum carbide surface layer has a hardness in the range of the order of 1500 to 1700 Vickers measured by micro-hardness at a load of 500 grams and a thickness of the order of from 10 to 300 microns.

15. A watch case element as claimed in claim 10 in which said surface layer has a colour which is the result of changing the chemical composition of the surrounding atmosphere in the course of heat-treating same.

16. A watch case element as claimed in claim 15 in which the colour is the result of changing the surrounding atmosphere following hardening thereof.

17. A watch case element as claimed in claim 15 in which the colour is the result of galvanic oxidation above 500° centigrade.

18. Method according to claim 3 characterized by the fact that the hardening is carried out for a duration of about 20 hours, at a temperature of about 1300°C.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,772,096 Dated November 13, 1973

Inventor(s) Charles Maquelin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the grant (only) cancel the two sheet of drawings bearing Patent No. 3,772,097. On the cover sheet [76] "Charles Maquelin, 16, chemin Gabriel, Peseux, Switzerland" should read -- Charles Maquelin, chemin Gabriel 2034 Peseux, Neuchatel, Switzerland --.

Signed and sealed this 16th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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