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(54) IMPROVEMENTS IN THE MANUFACTURE OF WATCH CASE ELEMENTS

(71) I, CHARLES MAQUELIN, a Swiss Citizen, of 16, Chemin Gabriel, 2034 Peseux, Neuchâtel, Switzerland, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of watch case elements and has for its object the provision of an improved method of manufacturing a watch case element.

In recent years, considerable research has been carried out in the watch-making industry in order to provide watch cases which have a hard surface which is also such as to maintain its pristine or newly-made appearance for as long as possible. A number of proposals have been made, including the use of sintered carbides, the use of stainless steel which is first hardened by nitriding and is then covered by a layer of hard chromium, the application of carbides to the surface of the watch case element by sputtering and also the use of an ordinary steel which is hardened by the vapour deposition of carbides.

All the proposals mentioned above have certain disadvantages. For example, one is very limited in the type of watch case one can make by a sintering process and the watch case elements so produced are very fragile. If the watch case element is made of stainless steel which is hardened by nitriding, the so hardened stainless steel has a reduced resistance to corrosion and it is therefore necessary to protect the stainless steel against corrosion by the application of a layer of chromium. The process is thus a multi-stage process and considerable difficulties are obtained as will be apparent to those skilled in the art.

When a carbide layer is applied by a sputtering process, the surface layer which one obtains is much too porous to enable one to obtain the type of surface which one

desires to obtain to facilitate polishing. Further, if ordinary steel is used which is hardened by the vapour deposition of metal carbides, a superficial layer is produced which has a hardness such that final polishing thereof is almost impossible.

Thus it is accordingly a more specific object of the present invention to provide a method of manufacturing a watch case element wherein a material is used which can be hardened as a final operation during the manufacturing procedure, the material used being, of course, non-magnetic, corrosion-resistant, easily machinable and capable of either hot or cold forming.

The method according to the invention is characterised in that the watch case element is formed of molybdenum and is hardened during the final manufacturing stage by carburisation so as to produce a surface layer of molybdenum carbide. The watch case element thus produced comprises molybdenum having a surface covering of molybdenum carbide.

Molybdenum has been shown to satisfy the requirements mentioned above and it is to be noted that the hardening of the watch case element during the final stage of manufacture does not comprise a cementation in the usual sense of this term, i.e. the formation of a very hard surface layer connected to the interior of the article by a transitional zone, but rather a carburisation process producing molybdenum carbide at the surface without the formation of any intermediaries.

The carburisation process is conveniently carried out by placing an otherwise finished watch case element in a container containing carbon powder, welding shut the container so as to effect a complete sealing thereof and then bringing the container and its contents to a temperature within the range of from 1100°C. to 1300°C. and holding it at that temperature for between ten and fifteen hours. The precise time for which carburisation is effected and the temperature at which

it is carried out in dependent on the thickness of the surface layer which one wishes to obtain; for layers of greater thickness, either the carburisation time or the carburisation temperature is increased.

Cooling of the thus treated watch case element must be effected at a controlled rate in a furnace and very slowly so as to ensure that the carbide layer does not become extremely fragile. Once the treated element has been cooled down to room temperature, one can re-heat it to a temperature of about 1000°C. and maintain it at that temperature for about two hours. If it is then cooled very slowly, diffusion of the formed molybdenum carbide into the molybdenum is effected so as to reduce the fragility of the element.

The hardness which is obtained is about 1500 to 1700 Vickers which is measured by micro-hardness with a load of 500 grammes, and the depth of carburisation is within the range of from 10 to 300 microns dependent on the carburisation temperature and carburisation time. The formed elements will not be deformed since the molybdenum at 1000°C. has the same resistance as iron at 20°C. and the nature of the surface layer is such that a simple polishing operation will give the formed elements the desired brilliant appearance.

The carburisation treatment can be carried out in a ceramic vessel containing carbon powder comprising 60% by weight of activated carbon, 30% by weight of powdered graphite and 10% by weight of powdered charcoal. In one particular example, using such material as the carburisation medium and carrying out carburisation for twenty hours at a temperature of about 1300°C., watch case elements were formed having a hard surface layer whose thickness was 150 microns and had a hardness of between 1500 and 1600 Vickers at a load of 500 grammes.

As an alternative to the carrying out of the carburisation process in a container filled with powdered carbon, a gaseous carburisation process can be effected, the watch case elements then being heated in a controlled atmosphere containing 98% hydrogen and 2% methyl alcohol.

In some cases it is desired to have a dark surface finish which has extreme brilliance and is readily polishable. Such colouring of the surface may be effected by heating the carburised elements in an atmosphere of hydrogen sulphide at a temperature of about 850°C. for about twenty minutes. Molybdenum disulphide is thus formed on the surface of the element.

Other colour treatments can be effected since molybdenum is quite readily oxidisable at a temperature above 500°C. Blue and orange colourings can be obtained by heat-

ing the molybdenum in a controlled oxidising atmosphere or by carrying out an anodic oxidation process using either an acid or an alkaline electrolyte.

WHAT I CLAIM IS:—

1. A method of manufacturing a watch case element, characterised in that the element is formed of molybdenum and is hardened during a final manufacturing stage by carburisation so as to produce a surface layer of molybdenum carbide.

2. A method according to claim 1, wherein carburisation is carried out by heating the element in carbon powder to a temperature within the range of from 1100°C. to 1300°C. for between ten and fifteen hours.

3. A method according to claim 1, wherein the carbon powder comprises 60% by weight of activated carbon, 30% by weight of powdered graphite and 10% by weight of powdered charcoal.

4. A method according to claim 1, wherein carburisation is carried out at a temperature at about 1300°C. for about twenty hours.

5. A method according to claim 1, wherein carburisation is carried out by heating the element in an atmosphere containing 98% hydrogen and 2% methyl alcohol.

6. A method according to any preceding claim, wherein, after carburisation, the element is re-heated to a temperature of about 1000°C., is maintained at that temperature for about two hours and is then cooled very slowly.

7. A method according to any one of claims 1 to 5, wherein, after carburisation, the element is treated in an atmosphere of hydrogen sulphide so as to form molybdenum sulphide on the surface of the element.

8. A method according to claim 7, wherein treatment of the element in the atmosphere of hydrogen sulphide is carried out at a temperature of about 850°C. for about twenty minutes.

9. A method according to claim 1, wherein, after carburisation, the colour of the element is modified by heating it in a controlled atmosphere.

10. A method according to claim 1, wherein, after carburisation, the colour of the element is modified by anodic oxidation.

it is carried out in dependent on the thickness of the surface layer which one wishes to obtain; for layers of greater thickness, either the carburisation time or the carburisation temperature is increased.

Cooling of the thus treated watch case element must be effected at a controlled rate in a furnace and very slowly so as to ensure that the carbide layer does not become extremely fragile. Once the treated element has been cooled down to room temperature, one can re-heat it to a temperature of about 1000°C. and maintain it at that temperature for about two hours. If it is then cooled very slowly, diffusion of the formed molybdenum carbide into the molybdenum is effected so as to reduce the fragility of the element.

The hardness which is obtained is about 1500 to 1700 Vickers which is measured by micro-hardness with a load of 500 grammes, and the depth of carburisation is within the range of from 10 to 300 microns dependent on the carburisation temperature and carburisation time. The formed elements will not be deformed since the molybdenum at 1000°C. has the same resistance as iron at 20°C. and the nature of the surface layer is such that a simple polishing operation will give the formed elements the desired brilliant appearance.

The carburisation treatment can be carried out in a ceramic vessel containing carbon powder comprising 60% by weight of activated carbon, 30% by weight of powdered graphite and 10% by weight of powdered charcoal. In one particular example, using such material as the carburisation medium and carrying out carburisation for twenty hours at a temperature of about 1300°C., watch case elements were formed having a hard surface layer whose thickness was 150 microns and had a hardness of between 1500 and 1600 Vickers at a load of 500 grammes.

As an alternative to the carrying out of the carburisation process in a container filled with powdered carbon, a gaseous carburisation process can be effected, the watch case elements then being heated in a controlled atmosphere containing 98% hydrogen and 2% methyl alcohol.

In some cases it is desired to have a dark surface finish which has extreme brilliance and is readily polishable. Such colouring of the surface may be effected by heating the carburised elements in an atmosphere of hydrogen sulphide at a temperature of about 850°C. for about twenty minutes. Molybdenum disulphide is thus formed on the surface of the element.

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ing the molybdenum in a controlled oxidising atmosphere or by carrying out an anodic oxidation process using either an acid or an alkaline electrolyte.

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2. A method according to claim 1, wherein carburisation is carried out by heating the element in carbon powder to a temperature within the range of from 1100°C. to 1300°C. for between ten and fifteen hours.

3. A method according to claim 1, wherein the carbon powder comprises 60% by weight of activated carbon, 30% by weight of powdered graphite and 10% by weight of powdered charcoal.

4. A method according to claim 1, wherein carburisation is carried out at a temperature at about 1300°C. for about twenty hours.

5. A method according to claim 1, wherein carburisation is carried out by heating the element in an atmosphere containing 98% hydrogen and 2% methyl alcohol.

6. A method according to any preceding claim, wherein, after carburisation, the element is re-heated to a temperature of about 1000°C., is maintained at that temperature for about two hours and is then cooled very slowly.

7. A method according to any one of claims 1 to 5, wherein, after carburisation, the element is treated in an atmosphere of hydrogen sulphide so as to form molybdenum sulphide on the surface of the element.

8. A method according to claim 7, wherein treatment of the element in the atmosphere of hydrogen sulphide is carried out at a temperature of about 850°C. for about twenty minutes.

9. A method according to claim 1, wherein, after carburisation, the colour of the element is modified by heating it in a controlled atmosphere.

10. A method according to claim 1, wherein, after carburisation, the colour of the element is modified by anodic oxidation.



11. An element of a watch case when manufactured by the method of any one of the preceding claims.
- 5 12. A method of manufacturing a watch case element according to claim 1 and substantially as hereinbefore described.
13. A watch case element manufactured by the method of claim 12.

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