

PATENT SPECIFICATION

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(54) GOLD DIFFUSION PROCESS AND SHAPED METAL ARTICLES

(71) We, TIMEX CORPORATION, a Corporation organized under the laws of the State of Delaware, United States of America, of Waterbury, Connecticut 06720, United States of America, 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:—

The present invention relates to a process of producing shaped heat hardened metal articles comprised of a base metal of copper alloy over which lies a covering of gold or gold alloy diffused into the base metal, and to such articles.

Various techniques have been employed in the past in the manufacture of articles from heat hardenable copper alloys which are diffusion coated with a noble metal. It has generally been found that it is unsuitable to coat the copper alloy prior to the shaping and finishing operation because of the physical changes which occur in the properties of the underlying body and the coating during the shaping and finishing operation. The thickness of the plated layer has often been found to change in forming steps after coating so that it varies in an irregular manner as well as disturbs the smooth finish of the coating metal producing a rough, uneven surface which is difficult to finish to an aesthetically acceptable degree. Excessive polishing and the like also diminish the thickness of the finished layer to an unacceptable degree.

In instances where the article has been plated before shaping and other fabrication steps, any cutting and the like will expose unplated portions to corrosion as well as ruining the aesthetic appearance of the article.

Various alternative approaches have been attempted to overcome these problems. One obvious approach is to form the shaped body of the base metal and apply the noble metal coating only after the shaping of the article has been completed. The adherence of the noble metal coating to the shaped body is then assured by diffusion heating which at first was carried out for short periods of time at rela-

tively high temperatures often within the softening range of the base metal or base metal alloy. In order to prevent the deformation of the article during high temperature diffusion heating, the treatment was carried out in a hot salt melt which unfortunately, however, often adversely affected the mechanical properties of the product. In cases where the noble metal was merely plated onto the underlying shaped base metal article and not diffused into the shaped base metal article by subsequent diffusion heat treatment, the coating lacked sufficient adherence to provide the desired durability and corrosion resistance.

In United States Patent Specification No. 3,157,539 a process is disclosed for making shaped metallic bodies having a noble metal coating wherein the underlying metal or alloy is one which is heat hardenable, and comprises shaping the object from heat hardenable copper alloy in its unhardened condition, and applying a coating of noble metal to the shaped body of the base metal which noble metal is adapted to be firmly joined to the shaped body of the copper alloy by diffusion heat treatment. The Patentee indicates that the underlying base metal is hardenable within a first temperature range, and that the heat diffusion process takes place within a higher second temperature range. The first and second temperature ranges partially overlap each other to define a third temperature range in which the formed and coated metal body is finally heated to simultaneously harden the underlying base copper alloy and diffuse the noble metal coating into the formed base metal. The process disclosed by the patentee comprises in effect a compromise between hardening the underlying metal at the preferred temperature range and simply adopting a single temperature range to carry out both processes simultaneously at the supposed third temperature range which is ideal neither for hardening nor diffusing. Thus, the final shaped and coated metal body has neither the best mechanical properties nor is the diffused coating as firmly adhered and uniformly diffused as desired. As indicated in the Patent, the temperature range

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at which the hardening and diffusing is simultaneously carried out ranges from 350°C to 600°C with a temperature of apparently 500°C being preferred. The base metal utilized in this Patent is copper or copper alloyed with beryllium or with silicon and manganese, or with silicon and nickel. The plating metal is gold or a gold alloy.

An additional difficulty which is encountered using some of the alloys previously employed in forming shaped metal articles mentioned is the difficulty in machining and shaping the article. This is believed due to the fact that most of the previous alloys employed in this type of manufacturing process have excluded free machining additives such as lead, selenium, tellurium or others.

A recent approach in this area to provide a shaped metal article of increased hardness and corrosion resistance has employed as the underlying metal a copper alloy which is a bronze comprised of copper, aluminium and nickel from which tin, zinc and lead have been excluded.

In one recent development, a bronze alloy of aluminium, nickel and copper has been electrically plated with about 4 microns of gold following machining. The machined workpiece was a watch bezel. After plating, the plated piece was simultaneously hardened and the gold layer diffused in a heat treatment.

It was thought necessary in this process to coat the gold diffused coating with a final coating of a hard metal such as chromium, rhodium or ruthenium to a thickness of approximately 20 microns because the diffused gold layer was not durable enough.

We have found that shaped metal articles of improved hardness, durability, corrosion resistance, and possessing improved finished appearance can be readily manufactured according to the process which we have discovered.

The process according to the invention of producing a shaped copper alloy body comprises the steps of shaping a heat hardenable copper alloy in the unhardened condition to a desired configuration, heating said heat hardenable copper alloy to a temperature of from 700°C to 900°C for 2 to 30 minutes and thereafter quenching said shaped metallic body thereby hardening said body and forming a eutectoid or transformed eutectoid and an alpha-crystalline phase structure, then coating at least a portion of the thus formed hardened shaped body with gold or gold alloy capable of forming a heat diffusion layer on said shaped metallic copper alloy body when subjected to diffusion-causing heat treatment, and thereafter heating said coated body to a temperature of from 400°C to 900°C for a period of from less than one minute to 30 minutes thereby diffusing said layer into said shaped copper alloy body.

The invention also provides a shaped metallic body comprised of a copper alloy base metal and a gold or gold alloy diffusion layer over said base metal, the shaped base metal body having been heat hardened prior to coating to establish a fine-grained eutectoid or transformed eutectoid and an alpha-crystalline phase, and having been heat treated subsequent to coating to cause the gold or gold alloy layer to diffuse into the base metal, and penetrate said base metal to a depth of at least 20 microns and with maximum concentration of the layer within the first 5 to 10 microns from the surface.

Shaped metal articles according to the present invention are utilized where the ultimate article being manufactured is one which requires good machineability properties, strength, durability and resistance to corrosion and discolouring. This invention is particularly concerned with the formation of shaped metal articles of the type described which serve a decorative function and which can be polished to a high degree of sheen such as watch bezels.

An improved gold diffusion coated shaped copper alloy article is provided by forming a copper alloy with chemical composition in the range 1 to 10% of aluminium and/or 0 to 10% of tin and optionally from 0 to 5% of free machining additives such as lead, selenium, tellurium, silicon, or others, remainder copper, into a desired shape and heating the shaped article to a temperature of from 700°C to 900°C and thereafter quenching the article at a controlled rate either in a gas or liquid quenchant. The shaped and hardened article is then coated, e.g. galvanically plated, with a layer of gold or gold alloy from 1 to 5 microns thick, although greater thicknesses may be employed if desired, and the gold coating diffused into the hardened copper alloy body by heating at a temperature from 400°C to 900°C for from less than one minute to 30 minutes, thereby diffusing the gold into the hardened base copper alloy. The process is particularly useful in forming watch bezels.

The heating and quenching of the shaped copper alloy article forms a fine-grained eutectoid or transformed eutectoid structure which is believed to enhance the rate and depth of diffusion and evenness of penetration of the gold layer. Gold coated hardened copper alloy particles of enhanced durability, resistant to corrosion, and having an aesthetically pleasing finish are obtained.

It is especially desirable that the article manufactured be relatively hard, resistant to dents, scratches and the like and have a durable and attractive coating of a noble metal which can be polished to a high sheen and is resistant to pits, scratches, discolouring and corrosion.

In a preferred embodiment, a watch bezel is shaped from copper alloy with chemical

composition of 7% aluminium, 7% tin and optionally up to 5% free machining additive such as lead, selenium, tellurium or others, remainder copper which is shaped and machined to the configuration of the watch bezel, heated to 900°C and quenched at a desired cooling rate by means of gas or liquid quench. The shaped article is then galvanically plated with a 5 micron layer of 24 carat gold and the plated article heated at 600°C for 15 minutes.

We have found that the preferred base copper alloy to employ is one which is comprised of aluminium, and/or tin with the balance copper. In order to enhance the machineability, another preferred alloy is one which comprises aluminium, tin and copper, plus from .1 to 5% free machining additives such as lead, selenium or tellurium, silicon, and others. A preferred range of free machining additives is 0.1 to 3% with 2 to 3% by weight most preferred. The alloying metals may range in amounts from approximately 1 to 10% for aluminium and 0 to 10% for tin. The preferred ranges are from 5 to 7% for both aluminium and tin, and from 0 to 3% free machining additives, with the balance copper. The most preferred composition of the alloy is one which is 7% aluminium, 7% tin plus approximately 3% of free machining additives, and the balance copper. Any appreciable amounts of nickel are excluded from the alloys employed according to the present invention.

Utilizing the copper alloys mentioned, we have found that the heating of the hardenable alloy prior to the coating step has been most effective when the shaped alloy and the machined alloy body has been heated to approximately from 700°C to 900°C, preferably about 900°C, for 2 to 30 minutes, and thereafter quenched at a controlled rate. The important point, however, depending upon the particular composition of the alloy utilized, is to quench from a temperature which will produce a fine-grained eutectoid or transformed eutectoid, since it is believed that it is the combination of the alpha-crystalline phase with the fine-grained eutectoid or transformed eutectoid which enhances the depth and effectiveness of the subsequent diffusion of the coated gold into the shaped structure.

We have found that the preferred temperature range for the diffusion step is from approximately 400 to 700°C, preferably 600°C, for from less than 1 minute to 15 minutes, and most preferred at temperatures of approximately 600°C for about 15 minutes. As indicated, the layer of gold applied can range from approximately 2 microns to 5 microns with about 4 microns being preferred. Tests following the diffusion step have indicated that the gold has diffused into the shaped structure to depths on the order of 50 microns although it is preferred to adjust the

process to concentrate a relatively high percentage of gold on the outer 5 to 10 microns from the surface, thus giving the optimum corrosion resistance.

As indicated above, while it does not appear to be necessary in order to obtain a hard, durable structure that is corrosion resistant, it is preferable to include up to about 3% by weight free machining additive in the heat hardenable copper alloy in order to enhance its machineability.

It is believed that the combination of the copper alloy together with the heat treatment prior to any coating with the gold or gold alloy produces a fine-grained eutectoid or transformed eutectoid structure which with an alpha crystalline phase leads to a controlled diffusion and increases the concentration across the diffused layer.

Also the diffusion is very rapid.

Examples of the Invention

Four samples of the alloy comprising 7% tin, 7% aluminium and the balance copper which had been shaped, machined into watch bezels, and heat treated by heating to 900°C and quenching as previously indicated were galvanically plated with 24 carat gold using conventional plating techniques. The samples were plated with approximately 2 microns of the gold. Thereafter the samples were heat treated as follows to diffuse the gold into the base metal structure.

Sample	Temperature	Time
1	600°C	less than 1 min.
2	600°C	5 min.
3	600°C	15 min.
4	750°C	less than 1 min.

Each sample produced a corrosion resistant hardened gold plated structure with gold diffused to a depth of at least 20 microns into the copper alloy base metal.

The foregoing procedures were repeated using base alloys having the following composition:—

- A. 5% aluminium, 5% tin, balance copper.
- B. 7% aluminium, 5% tin, balance copper.
- C. 5% aluminium, 7% tin, balance copper.

In each case, the alloy employed was free of the presence of any nickel. Equally good results were obtained.

The procedures above were repeated using alloys of varying composition within the scope of the invention for differing times and temperatures within the ranges disclosed.

The combination of the particular alloys and the initial heat treatment to form a eutectoid phase in the copper alloy enhances the hardening before application of the gold and greatly enhances the diffusion of the gold into the base alloy in terms of depth, evenness and time required.



WHAT WE CLAIM IS:—

1. A process of producing a shaped copper alloy body which comprises the steps of shaping a heat hardenable copper alloy in the unhardened condition to a desired configuration, heating said heat hardenable copper alloy to a temperature of from 700°C to 900°C for 2 to 30 minutes and thereafter quenching said shaped metallic body thereby hardening said body and forming a eutectoid or transformed eutectoid and an alpha-crystalline phase structure, then coating at least a portion of the thus formed hardened shaped body with gold or gold alloy capable of forming a heat diffusion layer on said shaped metallic copper alloy body when subjected to diffusion-causing heat treatment, and thereafter heating said coated body to a temperature of from 400°C to 900°C for a period of from less than one minute to 30 minutes thereby diffusing said layer into said shaped copper alloy body.

2. A process as claimed in Claim 1, which comprises adjusting conditions in the diffusion treatment to give maximum concentration of the gold or gold alloy diffusion layer within the first 5 to 10 microns from the surface.

3. A process as claimed in Claim 1 or Claim 2, wherein said copper alloy is nickel free and comprises from 1 to 10% by weight of aluminium and 0 to 10% by weight tin, the balance being copper.

4. A process as claimed in Claim 3 wherein said copper alloy comprises from 5 to 7% by weight each of aluminium and tin, the balance being copper.

5. A process as claimed in Claim 3 wherein said copper alloy comprises approximately 7% by weight tin, 7% by weight aluminium, the balance being copper.

6. A process as claimed in any one of the preceding claims, wherein said copper alloy further comprises 0.1 to 3% by weight of lead, selenium, tellurium, silicon, or other free machining additive.

7. A process as claimed in any one of the preceding claims, wherein said gold or gold alloy is coated onto said shaped copper alloy body galvanically to a thickness of from 1 to 5 microns.

8. A process as claimed in any one of the preceding claims, wherein said heat diffusion step is carried out at a temperature of about

600°C for from less than one minute to 15 minutes.

9. A process as claimed in any one of the preceding claims, wherein the quenching is carried out in gas or liquid.

10. A process as claimed in any one of the preceding claims, wherein the first heating step is carried out at approximately 900°C and the second heating is carried out at approximately 600°C for from less than one minute to 15 minutes.

11. A shaped metallic body comprised of a copper alloy base metal and a gold or gold alloy diffusion layer over said base metal, the shaped base metal body having been heat hardened prior to coating to establish a fine-grained eutectoid or transformed eutectoid and an alpha-crystalline phase, and having been heat treated subsequent to coating to cause the gold or gold alloy layer to diffuse into the base metal, and penetrate said base metal to a depth of at least 20 microns and with maximum concentration of the layer within the first 5 to 10 microns from the surface.

12. An article as claimed in Claim 11 wherein said copper alloy comprises from about 1% to about 10% by weight of aluminium and from 0 to 10% by weight of tin, the balance being copper.

13. An article as claimed in Claim 12 wherein said aluminium and tin comprise from 5 to 7% by weight, the balance being copper.

14. An article as claimed in Claim 13 wherein the alloy is comprised of 7% aluminium, 7% tin, 3% lead or other free machining additive, and the balance copper.

15. An article as claimed in any one of Claims 11 to 14, wherein said base metal copper alloy is nickel free.

16. A shaped metallic body substantially as hereinbefore described with reference to the Examples.

17. A process of producing a shaped heat hardened base metal copper alloy article having a diffused gold or gold alloy coating, according to Claim 1 and substantially as hereinbefore described.

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