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COMPOSITE SILVER AND COPPER ARTICLE

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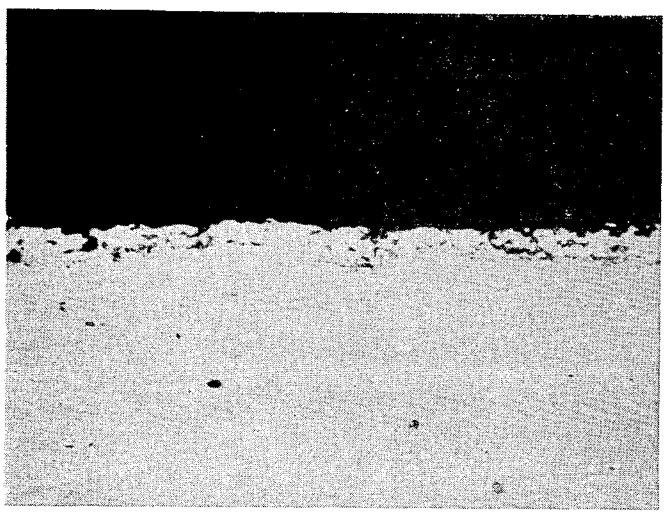

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3,419,364
COMPOSITE SILVER AND COPPER ARTICLE
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Original application June 24, 1965, Ser. No. 466,647, now Patent No. 3,372,468, dated Mar. 12, 1968. Divided and this application Sept. 1, 1967, Ser. No. 695,297
5 Claims. (Cl. 29—183.5)

ABSTRACT OF THE DISCLOSURE

A composite alloy having a core consisting essentially of from 10 to 70% silver and the balance copper clad with a surface layer consisting essentially of a silver copper alloy matrix wherein the matrix is at least 91% silver with the balance copper, said matrix containing discrete islands in an amount less than 5% of the cladding and wherein these islands contain less than 8% silver.

This application is a division of copending application Ser. No. 466,647, filed June 24, 1965, now Patent 3,372, 468.

The present invention relates to a process for producing new and improved silver-copper alloys and to the alloys produced thereby.

Considerable time and effort is currently being expended on the production of silver alloys containing reduced amounts of silver while retaining surface appearance and characteristics of those alloys containing greater amounts of silver. For example, it is recognized that a need exists for reducing the amount of silver present in coinage metal while retaining the surface appearance and physical characteristics of the current silver-containing coinage metal. Currently, coinage metal contains about 90% silver and 10% copper and is characterized by a distinctive white appearance. When the alloy is debased to contain, for example, around 40% silver and the balance essentially copper, an alloy which has been proposed for coinage use, acceptable physical characteristics are attained with the disadvantage that the alloy is brass-like in color as opposed to the desirable white appearance of the present 90% silver, 10% copper coinage metal.

In addition there are many other applications where it would be highly desirable to obtain a debased silver alloy having physical characteristics and appearance of high silver-containing alloys, for example, sterling silver. The term "sterling silver" is intended to imply any alloy containing at least 91% silver and the balance essentially copper. Examples of other uses for such a debased silver alloy include decorative uses, utensils of various types, and so forth.

It is, therefore, a principal object of the present invention to provide debased silver alloys and a method for preparing said alloys, which alloys retain the physical characteristics and surface appearance of alloys containing at least 90% silver.

It is a further object of the present invention to provide a method and improved alloys as aforesaid wherein the alloys contain substantially less silver than current coinage metal while generally retaining physical characteristics and surface appearance of current coinage metal.

It is an additional object of the present invention to provide a process and alloys as aforesaid which are based on a silver-copper alloy system.

It is a further object of the present invention to achieve the foregoing objects simply and conveniently at relatively low cost.

Further objects and advantages of the present invention will appear hereinafter.

It has now been found that in accordance with the present invention the foregoing objects and advantages may be readily achieved.

The process of the present invention comprises: providing an alloy consisting essentially of from 10 to 70% silver and the balance essentially copper; heating said alloy in an oxidizing environment, preferably air, for at least 30 minutes at a temperature above the decomposition temperature of silver oxide and below 780° C., thereby forming a surface layer of at least 0.1 mil in depth containing copper oxides and a silver rich alloy containing over 91% silver, balance copper, and discrete islands of copper containing less than 8% silver in solid solution; and removing copper oxides from said surface layer. The alloy may be so treated on all external surfaces or on only part thereof if desired. If only portions of the external surfaces are sought to be treated, those surfaces to be untreated are suitably masked.

The copper oxides are a mixture of mainly cupric oxide plus small amounts of cuprous oxide, generally about 95% cupric oxide and 5% cuprous oxide.

The above process surprisingly readily achieves all of the foregoing objects of the present invention.

The result of the process of the present invention is a debased silver alloy achieving the highly desirable goal of reduced silver content with the retention of the characteristic white surface appearance of the high silver-containing coinage metal. The alloy of the present invention is in effect a composite alloy characterized by a core consisting essentially of from 10 to 70% silver and the balance essentially copper and a white colored, copper depleted surface layer of a depth of at least 0.1 mil containing at least 91% silver, balance copper. The surface layer contains, in addition to the foregoing silver rich alloy, discrete islands of copper containing less than 8% silver in solid solution. These discrete islands generally make up less than 5% of the surface layer, with the silver rich alloy making up over 95%. This white colored, copper depleted surface layer is obtained by leaching out the copper oxides after the heat treatment oxidation step. The white colored surface layer is always alpha phase in contrast to the core which contains alpha phase, i.e., grains of silver rich alloy, and beta phase, i.e., grains of copper rich alloy. The composite shows a sharp transition from the alpha plus beta of the core to the alpha of the cladding, with no transition zone.

Generally in addition to the foregoing discrete islands the cladding contains from 92 to 96% silver, balance copper.

In accordance with the process of the present invention the composite is prepared from a single alloy. The alloy which is utilized as starting material consists essentially of from 10 to 70% silver and the balance essentially copper. It is preferred to utilize from about 30 to 45% silver as this is the range currently being considered for coinage metal. Naturally, the present invention contemplates the use of small amounts of additional alloying substituents to obtain desirable physical characteristics, such as aluminum, iron, nickel, cobalt, lead, palladium, platinum, tin, zinc, magnesium, lithium, phosphorus, etc.

Naturally, the present invention contemplates the use of conventional impurities typical in alloys of this type.

The present invention is not dependent upon form of the particular alloy. The desirable features of the present invention are obtainable irrespective of the form in which the alloy is provided. The method by which the starting material is formed is immaterial. For example, the present invention is applicable to starting materials which are powder pressed, cast or wrought, i.e., rolled, drawn, forged, chased, etc.

In accordance with the present invention the foregoing alloy is heated in an oxidizing environment at a temperature above the decomposition temperature of silver oxide but below 780° C. The preferred oxidizing environment is naturally air but others can be used if desired, for example, pure oxygen or air enriched with oxygen. By decomposition temperature of silver oxide it is intended to signify the decomposition temperature of silver oxide at atmospheric pressure.

The foregoing heating step selectively oxidizes surface copper to copper oxides while leaving the silver component unchanged. The depth to which the copper can be oxidized is naturally dependent upon the specific temperature employed and the duration of the oxidizing treatment and the nature of the oxidizing environment. The depth of the surface layer is at least 0.1 mil and it is normally preferred to oxidize a surface layer of from ½ mil to 5 mils in depth. Naturally, longer treatment times and higher temperatures and greater oxidizing power in the oxidizing environment results in greater depths of oxidation of the copper. It is not necessary to oxidize all surface copper to copper oxide, it is preferred, however, that the surface copper be substantially oxidized to copper oxide.

Broadly, the oxidizing temperature of the present invention is from 350° C. to 780° C. Temperatures above 780° C. are inappropriate as above 780° C. incipient melting will occur. The preferred oxidizing temperature is from 400 to 780° C., with the optimum temperature being from 600 to 725° C. The 600 to 725° C. temperature range generally yields a surface coating corresponding to commercial sterling silver. The optimum temperature range is also due to the fact that it has been found that this temperature range is the most effective in producing thicker, less porous and more wear resistant surface layers.

It is preferred in accordance with the present invention to combine the heating step with an annealing step that is necessary in the processing of the dilute silver-copper alloys. Therefore, in the preferred embodiment the alloys are simultaneously heated in the foregoing manner and annealed for at least 30 minutes. This has the particular advantage of combining a process step with a step which is necessary in the processing of these alloys.

Following the selective oxidation of surface copper to copper oxides, while leaving the silver component of the alloy unchanged, the copper oxides can be removed from the surface layer by any desired means. It is preferred to remove the copper oxides by etching in any of a variety of chemicals which dissolve copper oxides but have less attack on the silver, for example, dilute sulfuric acid or nitric acid solutions. Sulfuric acid solutions are particularly preferred for this treatment. Alternatively, the copper oxides can be removed by reductive dissolution. This comprises forming a cell by making the specimen cathode in a buffered, weakly acid solution with, for example, a steel anode. Hydrogen ions move towards the cathode causing reduction of cupric to cuprous and ultimate dissolution and removal of the oxide.

The preferred method is simply to immerse the specimen in one normal sulfuric acid for about 5 minutes at room temperature.

After removal of the copper oxides from the surface layer, the alloy is a composite alloy characterized by a core corresponding in composition to the original alloy with a surface layer to the desired depth depleted in copper. The surface layer is rich, white in color and is characterized chemically as indicated hereinabove.

It is not necessary to remove all of the copper oxides from the surface of the alloy, but only that amount which is required to restore the pleasing, white appearance of the silver itself. Thus depletion of the copper content in the surface layer need not be carried out to completion since silver alloys containing small amounts of copper in the surface layer will retain a white appearance.

After removal of the copper oxides the resultant composite can be cold or warm rolled up to about 780° C. In fact, it is preferred to compact the somewhat porous surface layer by any desired means, for example, rolling, stamping, forging, coining, chasing, drawing, etc.

The process and alloys of the present invention will be more readily apparent from the consideration of the following illustrative examples.

EXAMPLE I

An alloy was prepared to contain about 60% copper and 40% silver. The alloy was prepared by melting together the silver and copper substituents at about 1000° C. followed by chill casting into a steel mold of 1¼ by 1¼ inches.

The ingot was scalped and cold rolled to about one-eighth of an inch in thickness followed by annealing at 650° C. for 30 minutes, followed by cold rolling to a thickness of 0.060". The specimen was then heated for 30 minutes in air at 700° C. followed by acid pickling by immersing in a dilute, one normal sulfuric acid solution for about 5 minutes. This resulted in a composite having a core corresponding to the original composition of the alloy and containing both alpha plus beta phase, i.e., containing both grains of silver rich alloy and grains of copper rich alloy.

The cladding, on the other hand, was a rich, white color and contained only alpha phase, i.e., a silver rich alloy containing over 91% silver, balance copper and discrete islands of copper containing less than 8% silver in solid solution. The cladding was 0.00048" thick (about one-half mil).

The composite alloy is shown on the attached photomicrograph shown at a magnification of 500×. In the photomicrograph the core and clad layers can be clearly seen. In the clad layer, the openings are pores or inclusions of oxide and/or copper alloy.

EXAMPLE II

The composite alloy prepared in Example I was cold rolled with a light, skin pass. The skin pass did not significantly elongate the specimen, but simply compacted the cladding to about one-half of its original thickness.

EXAMPLE III

The procedure of Example I was repeated, except that instead of heating in air for 30 minutes, the specimen was heated in air for 2 hours. This resulted in a composite having the same characteristics as in Example I except that the cladding layer had a thickness of about one mil.

EXAMPLE IV

The composite alloy prepared in Example III was cold rolled with a light, skin pass. Tht skin pass did not significantly elongate the specimen, but simply compacted the cladding to about one-half of its original thickness.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not retsrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A composite alloy having a core consisting essentially of from 10 to 70% silver and the balance essentially copper clad with a white colored, copper depleted surface layer of at least 0.1 mil. in depth conesisting essentially of a silver copper alloy matrix which is at least 95% of the cladding and wherein the matrix is at least 91% silver with the balance copper, said matrix contain-

ing discrete islands of a copper-silver alloy which islands are less than 5% of the cladding and wherein the silver in these islands is less than 8% of this constituent.

2. An alloy according to claim 1 wherein said surface layer is from 0.5 to 5 mils in depth.

3. An alloy according to claim 1 wherein said silver rich alloy contains from 92 to 96% silver, balance copper.

4. An alloy according to claim 1 wherein said core is alpha plus beta phase and said cladding is alpha phase.

5. An alloy according to claim 1 wherein said core contains from 30 to 45% silver, balance essentially copper.

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