The instant disclosure teaches an improved article consisting essentially of a white copper base alloy plated with a silver plating, wherein the white copper base alloy consists essentially of nickel from 0.5 to 5 percent, zinc from 15 to 35 percent, manganese from 5 to 20 percent, balance copper, wherein the total of manganese plus zinc cannot exceed 40 percent. The article of the present invention is particularly desirable for articles of flatware or hollow ware.

9 Claims, No Drawings
PLATED COPPER BASE ALLOY ARTICLE
CROSS REFERENCE TO RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

The nickel-silvers are commonly used for flatware and hollow ware applications. In general, these articles are silver plated and benefit considerably from the white alloy substrate. For example, the shiny white base enhances the luster of the finished product. In addition, should the silver plating wear off, the white alloy exposed at the surface blends with the remaining silver plate. The nickel-silvers, however, present certain undesirable features. In the first place, it is desirable to develop a material which can be used for these applications which is less expensive than conventionally used nickel-silvers, particularly in view of the high cost of nickel. Furthermore, in addition to the high cost of nickel, the nickel-silvers are difficult to fabricate with respect to hot rolling. The hot rolling temperature range is narrow and high. This is not only expensive processing, but necessitates the use of smaller ingots.

Still further, articles of flatware, for example, are generally formed by rolling to shape and coining to provide the pattern. The finished article is then silver plated. A prime requirement for coinability is low hardness. A fine grain size is essential to provide the bright finish silver plated article. In the nickel-silvers, however, it is not possible to provide a low hardness with the desired fine grain size.

Furthermore, articles of hollow ware, for example, are frequently drawn or stretched formed. Such articles are often made from brass or other nonwhite alloys due to the limited drawability and formability of the low nickel-silvers. Hollow ware articles formed from materials of this type must be nickel plated prior to silver plating, with an attendant increase in cost.

Accordingly, it is a principal object of the present invention to provide an improved silver plated article.

It is a further object of the present invention to provide an improved silver plated article which utilizes a relatively inexpensive white copper base alloy as a substitute for the conventionally used nickel-silvers.

It is a still further object of the present invention to provide an improved silver plated article which may be conveniently and inexpensively used in articles of flatware or hollow ware.

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

SUMMARY OF THE INVENTION

In accordance with the present invention it has now been found that the foregoing objects and advantages may be readily achieved. The article of the present invention consists essentially of a white copper base alloy plated with a silver plating having a thickness of from 0.0001 to 0.010 inch, wherein the white copper base alloy consists essentially of nickel from 0.5 to 5 percent, zinc from 15 to 35 percent, manganese from 5 to 20 percent, balance copper, wherein the total of manganese plus zinc cannot exceed 40 percent. The article of the present invention is particularly useful in articles of flatware or hollow ware.

In accordance with the present invention, numerous highly significant advantages are achieved. The copper base alloys which are utilized have a desirable white color which enhances the luster of the finished product and, should the silver plating wear off, the white alloy exposed at the surface readily blends with the remaining silver plate. Furthermore, the copper base alloys used herein are particularly desirable as a replacement for the conventionally used nickel-silvers in view of the high cost of nickel and also in view of the fact that the copper base alloys used herein are more readily fabricated than conventional nickel-silvers. These copper alloys have properties comparable to the nickel-silvers and are more easily fabricated.

Further advantageous features of the articles of the present invention will appear hereinafter.

DETAILED DESCRIPTION

As is indicated hereinafore, the articles of the present invention consist essentially of the foregoing white copper base alloys plated with a silver plating. The copper base alloys used herein are readily cast and rolled. In casting the alloys, there is a criticality in pouring temperature because of the fluidity of the melt due to the presence of manganese. The pouring temperature must be maintained below 1100°C. In addition, the manganese addition must be followed by the addition of one of the alloying elements, such as copper or cupro nickel or zinc or nickel in order to submerge the manganese or one might have heavy loss of manganese by preferential oxidation. Other than the foregoing, the copper alloys are readily processed. The alloys are readily hot rollable in contrast to the nickel-silvers which are hot rollable only over a limited temperature range. Low finishing temperatures, below 800°C, lead to edge cracking with respect to the nickel-silvers. Since the nickel-silvers have a very limited temperature range over which they can be hot rolled without edge cracking and since the ingot is continuously losing temperature during the hot rolling process, only substandard lengths of the nickel-silvers can be processed. This is not so with respect to the present alloys. For example, the instant copper alloys may be hot rolled over the broad temperature range of from 840°C to 480°C without difficulty.

Furthermore, the copper alloys may be cold rolled in excess of 90 percent without edge cracking between interanneals.

Of course, it should be noted that all of the foregoing significant advantages are obtained at a lower cost than commonly used nickel-silvers.

As stated hereinafore, the copper alloys contain from 15 to 35 percent zinc. The preferred zinc content is from 28 to 33 percent. The nickel content of the alloys is from 0.5 to 5 percent and preferably from 3 to 5 percent as this gives higher strength and formability. The manganese content is from 5 to 20 percent and preferably from 5 to 12 percent. The balance of the alloy is essentially copper.

When manganese is used in amounts over 20 percent, this lowers the solidus temperature so that there is
3,778,236

more difficulty in casting and hot rolling. Zinc contents over 35 percent yield some beta phase at room temperature which reduces cold rollability and corrosion resistance. Naturally, increasing the nickel content will increase the cost.

In accordance with the present invention, the total of manganese and zinc cannot exceed 40 percent of the alloy. In general, the higher the manganese content the lower the zinc content since both tend to promote undesirable second phases and lower the solidus temperature.

Naturally, the present invention contemplates the use of small amounts of additional alloying ingredients to, for example, improve mechanical properties or corrosion resistance in the instant copper alloys. In general, less than 0.3 percent of each of the following materials may be added. Preferably less than 0.3 percent each is employed, in order to avoid undesirable second phases and avoid fabrication problems. For example, if too much aluminum is added, e.g., 1 percent, there is formed beta phase and some nickel-aluminum phase. This results in edge cracking when hot rolled and markedly reduces the limit of cold rollability and raises the recrystallization temperature. Other elements which may be added include aluminum, iron, tin, silicon, cobalt, magnesium and molybdenum. Phosphorus, arsenic, and antimony may be added up to 0.3 percent. Lead may be added in quantities up to 3 percent in order to improve machinability.

Small amounts of the foregoing alloying additions may be readily used, if desired, for example, 0.001 percent each.

Naturally, the alloys of the present invention may contain common impurities up to 0.05 percent each, total 0.25 percent.

Throughout the instant specification all percentages are weight percentages.

In accordance with the present invention, the instant alloys may be readily processed.

The alloys may be readily hot and cold rolled. As stated hereinabove, the alloys are hot rolled over a broad temperature range from 840°C to 480°C and may be cold rolled in excess of 90 percent without edge cracking and with no interanneals required. This is a significant advantage. Naturally, if desired, the alloys may be given intermediate anneals at 450° to 700°C and preferably 525 to 675°C for at least 15 minutes and preferably one to four hours. A plurality of cycles of cold rolling and annealing may be employed. In fact, it has been surprisingly found in accordance with the present invention that one or more cycles of cold rolling and annealing obtains a broad range of hardnesses for specific grain sizes. Normally, this variability of hardnesses is not obtainable for specific grain sizes.

The alloys may be subjected to a final anneal in order to render them in the optimum condition for high formability. The annealing temperature is in the range of 300° to 700°C and preferably 525° to 675°C. An annealing time of at least 15 minutes is necessary and the preferred annealing time is one half to four hours.

An additional advantage of the processing of our invention is the resultant improvement in limiting draw ratio (LDR). Generally, this defines the amount of deep drawing which can be put into a particular sample without intermediate anneals. Naturally, it is highly desirable commercially to have a higher LDR. This is particularly desirable in fabricating hollow ware articles.

The resultant alloys are single phase alpha alloys at room temperature. This leads to the virtually unlimited cold rollability thereof. The alloys have highly desirable physical properties. For example, in the cold rolled condition, 50 to 70 percent cold rolled, the yield strength ranges from 95 to 115 ksi, ultimate strength 105 to 130 ksi, and elongation 1 to 12 percent. The annealed properties are as follows: yield strength, 20 to 60 ksi, ultimate strength 55 to 80 ksi, and elongation 25 to 60 percent.

The silver plated article of the present invention may be formed by conventional procedures known in the art. Any convenient or suitable process may be readily employed. Naturally, the exact plating procedure will vary depending upon the particular article to be prepared. The following represents a typical procedure which may be conveniently utilized.

A typical article for silver plating would be processed from annealed copper alloy strip of the present invention. A blank is first formed, for example, utilizing a punch and die set, roughly in the shape of the final product. The blank may be cross rolled and/or grade rolled to provide any required taper, for example, for an article of flatware. An annealing step may be interposed between the two rolling operations, if desired. The profile or exact shape of the article may then be cut from the blank, which step may be followed by an annealing operation, if desired. The final forming operation may then be performed, including the application of pattern. The article is then trimmed, buffed and/or polished preparatory to plating. Also, a variety of cleaning and rinsing procedures may obviously be utilized prior to plating.

After cleaning and prior to electroplating with silver, the article should be struck with silver. This is basically a mild or extremely thin electroplating operation. The articles may also be struck with nickel prior to the silver strike. A typical silver striking bath includes silver cyanide and potassium cyanide, with optional additives, such as potassium carbonate and copper cyanide. A typical nickel striking bath includes nickel chloride, NiCl₂ · 6H₂O and hydrochloric acid.

Articles of the type of the present invention are then commonly electroplated with silver to the desired plating thickness from a cyanide bath. The baths utilize a silver anode and may contain brighteners, such as carbon disulfide or ammonium thiosulfate. Typical plating procedures utilize temperatures from 75° to 125°F and current densities in the range of 5 to 150 amps per square foot. The resultant plated article may then be polished as desired.

A particular advantage of the silver plated articles of the present invention is found in flatware and hollow ware applications. As a result of the surprising characteristics of the copper base alloys which are used herein, it is possible to achieve both a fine grain size and a low hardeness and thus provide a superior substrate for silver plated flatware articles. In articles of hollow ware, the present invention overcomes the disadvantage of conventionally used brass or other non-white alloys which must be nickel plated prior to silver plating. The copper alloys used herein provide a white alloy which exhibits drawability and formability equivalent or superior to brass. It is, therefore, possible to produce articles of silver plated hollow ware at a greatly reduced cost.
Although the present invention is particularly useful in preparing silver plated flatware and hollow ware articles, the present invention finds application in any silver plated article in view of the surprising characteristics thereof as described hereinabove.

The present invention and improvements resulting therefrom will be more readily understandable from a consideration of the following illustrative examples.

**EXAMPLE I**

Alloys were prepared using DC casting of 5 ¼ inches × 28 ¾ inches × 25 feet dimensions with a pouring temperature of 1050°C. Manganese was added as electrolytic flakes, pure zinc was added, the manganese addition preceded a heavy dosage of a copper nickel master alloy, and copper and nickel were added as master alloys. The casting was done under a charcoal cover. The alloys prepared had the following composition wherein all ingredients are expressed in weight percentages.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Manganese</th>
<th>Zinc</th>
<th>Nickel</th>
<th>Tin</th>
<th>Iron</th>
<th>Lead</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.1</td>
<td>29.75</td>
<td>4.95</td>
<td>&lt;0.02</td>
<td>0.025</td>
<td>&lt;0.008</td>
<td>Balance.</td>
</tr>
<tr>
<td>B</td>
<td>6.6</td>
<td>28.20</td>
<td>4.80</td>
<td>&lt;0.02</td>
<td>&lt;0.03</td>
<td>&lt;0.008</td>
<td>Balance.</td>
</tr>
</tbody>
</table>

**EXAMPLE II**

The alloys prepared in Example I were processed in the following manner. The alloys were hot rolled from 825°C down to 600°C on a single stand, reversing hot mill. The alloys were then cold rolled down to 5.25 inches to 0.040 inch in eleven passes. The alloys were then readily cold rolled in two passes down to a gage of 0.160 inch on a two stand, tandem cold mill. There were no signs of edge cracking in the cold rolled sheet. The alloys were then annealed at a temperature of 625°C to 650°C for three hours. The alloys had the following properties.

**EXAMPLE III**

Alloy A prepared in Example I was processed in a manner after Example II in the following manner. The alloy was hot rolled from 5.25 inches to 0.400 inch from 825°C down to 600°C and coil milled to 0.365 inch. The material was cold rolled to approximately 0.185 inch and annealed for one hour at 625°C, further cold rolled to approximately 0.100 inch and finally annealed at 625°C for one hour. The Rockwell - B hardness of the annealed strip was 39 and the finish grain size was approximately 0.040 mm.

**EXAMPLE IV**

A spoon was manufactured from the Alloy A strip as prepared in Example III in the following manner. A blank was formed utilizing a punch and die such that the blank was roughly in the shape of the final product but had a rectangular "bowl". The bowl portion of the spoon was cross rolled approximately 20 percent to a thickness approximately 0.080 inch. The bowl section was then grade rolled to provide a taper varying from a thickness of 0.080 inch to approximately 0.040 inch. Following this the exact shape of the spoon was cut out. Next the bowl was formed and a pattern was struck on the handle. The unplated spoon was trimmed, cleaned and buffed preparatory to plating.

**EXAMPLE V**

The spoon blank as prepared in Example IV was processed for electroplating by striking with silver using an aqueous striking bath containing silver cyanide in an amount of 0.9 oz. per gallon and potassium cyanide in an amount of 10.0 oz. per gallon. A temperature of 75°F was utilized at a current density of 30 amps per square foot and less than six volts. A steel anode was employed. The blank was immersed in the bath for the period of time of less than one minute.

**EXAMPLE VI**

The spoon blank bearing the silver strike as prepared according to Example V was then electroplated with silver utilizing an aqueous silver plating bath containing the following ingredients: silver cyanide, 4.8 oz. per gallon; potassium cyanide, 8.0 oz. per gallon; potassium carbonate, 6.0 oz. per gallon; and carbon disulfide, 0.0001 oz. per gallon. A silver anode was employed, the temperature was maintained in the range of 75°F – 90°F and the current density in the range of 5 – 15 amps per square foot and less than six volts. The plating time was adjusted so that the final plating thickness was approximately 0.001 inch. The plated article was finally polished in the conventional manner. 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 restrictive, 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. An article consisting essentially of a white copper base alloy plated with a silver plating having a thickness of from 0.0001 to 0.010 inch, wherein the white copper base alloy consists essentially of nickel from 0.5 to 5 percent, zinc from 15 to 35 percent, manganese from 5 to 20 percent, balance copper, wherein the total of manganese plus zinc cannot exceed 40 percent.

2. An article according to claim 1 wherein said article is an article of flatware.
3. An article according to claim 2 including a pattern coined thereon.

4. An article according to claim 1 wherein said article is an article of hollow ware.

5. An article consisting essentially of a white copper base alloy plated with a silver plating having a thickness of from 0.0001 to 0.010 inch, wherein the white copper base alloy consists essentially of nickel from 0.5 to 5 percent, zinc from 15 to 35 percent, manganese from 5 to 20 percent, from 0.001 to 0.3 percent of a material selected from the group consisting of phosphorus, arsenic and antimony, balance copper, wherein the total of manganese plus zinc cannot exceed 40 percent.

6. An article consisting essentially of a white copper base alloy plated with a silver plating having a thickness of from 0.0001 to 0.010 inch, wherein the white copper base alloy consists essentially of nickel from 0.5 to 5 percent, zinc from 15 to 35 percent, manganese from 5 to 20 percent, from 0.001 to 0.3 percent of at least one material selected from the group consisting of aluminum, iron, tin, silicon, cobalt, magnesium, molybdenum and mixtures thereof, balance copper, wherein the total of manganese plus zinc cannot exceed 40 percent.

7. An article according to claim 1 wherein said copper alloy contains lead in an amount from 0.001 to 3 percent.

8. An article according to claim 1 wherein said copper alloy contains impurities in an amount up to 0.05 percent each, total 0.25 percent.

9. An article according to claim 1 wherein said copper alloy contains nickel in an amount from 3 to 5 percent, zinc in an amount from 28 to 33 percent and manganese in an amount from 5 to 12 percent.

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