

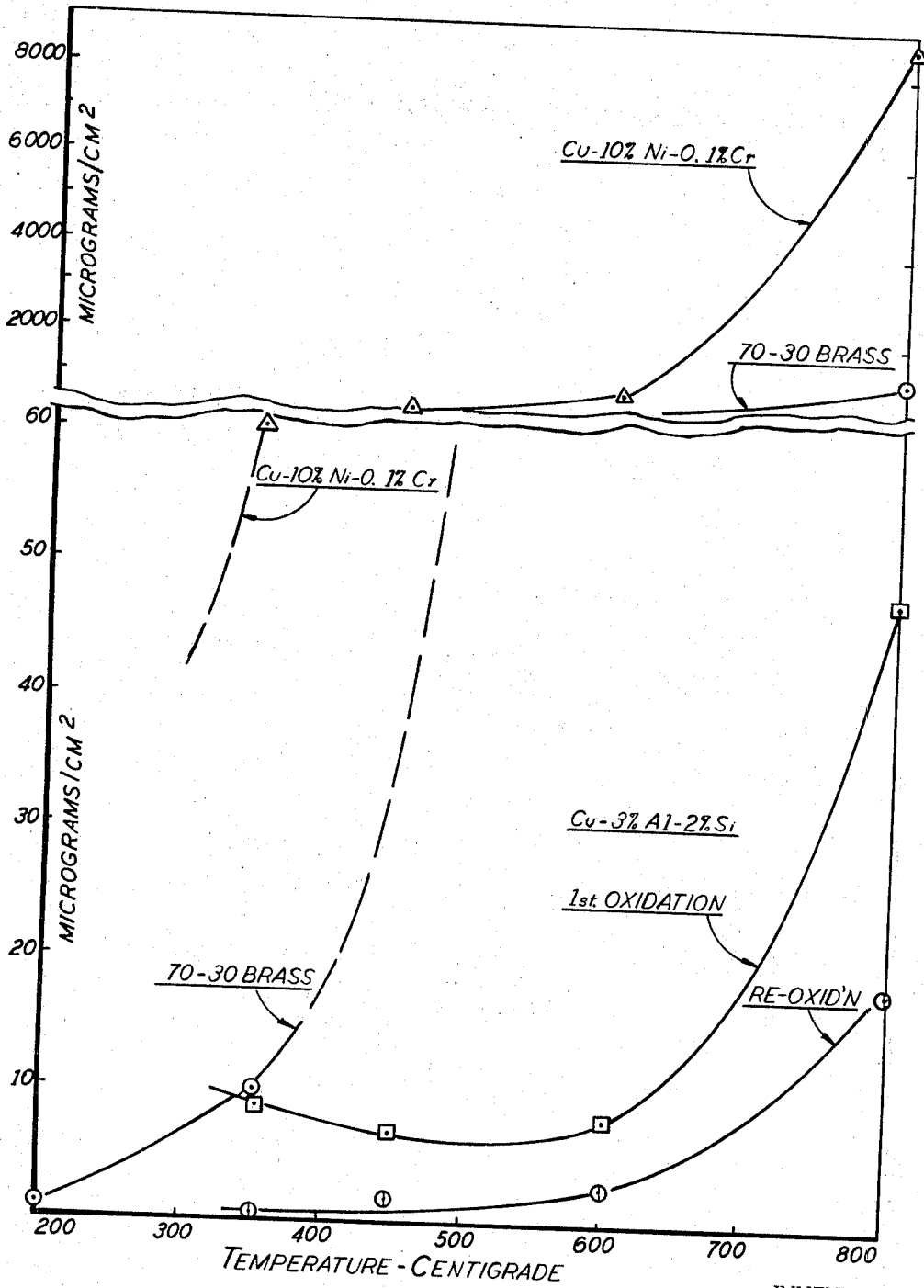
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COPPER BASE ALLOYS AND PROCESS FOR PREPARING SAME

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COPPER BASE ALLOYS AND PROCESS FOR PREPARING SAME

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ABSTRACT OF THE DISCLOSURE

The present invention relates to new and improved copper base alloys having substantially improved resistance to oxidation and tarnishing in moist and contaminated atmospheres and the process for preparing said alloys said alloy having an oxidation resistant zone of at least 50 Angstroms in depth consisting of a discrete dispersion of oxide in the metal matrix.

Copper base alloys have found wide and varied uses in industry and commerce in general; however, the many useful physical properties of these alloys are almost invariably negated to some degree by their extremely low resistance to oxidation and to tarnishing, especially in moist and contaminated atmospheres. This poor oxidation resistance has limited the utility of copper base alloys and has resulted in long and continuing efforts to overcome this disadvantage.

It has long been the object of the copper industry to develop new copper base alloys which overcome these disadvantages and are characterized by good oxidation resistance. The copper industry has aimed to develop new copper base alloys whose resistance to oxidation and tarnishing is at least as good as austenitic stainless steels. The previous approach to this problem has been the investigation of the oxidation and tarnishing characteristics of binary copper alloys where the binary alloying addition is strongly reducing in nature and which, by itself, grows highly protective oxidation films, for example, aluminum. This approach has been unsuccessful in attaining stainless properties which are self-healing in everyday environments.

There has been some limited success where the binary alloys were processed in such a manner as to completely prevent the oxidation of the copper matrix while still permitting oxidation of the alloying addition, see, for example, Journal of the Institute of Metals, 63, 21 (1938), by L. E. Price and G. T. Thomas. This result has been usually attained by selective oxidation whereby the binary alloys are subjected to high temperature treatment in atmospheres, such as moist hydrogen, which will oxidize the reducing alloying ingredient but which maintains the copper, with its lower free energy of oxidation, in the reduced condition. This type of treatment often produces protective, invisible, oxide films of the alloying addition. These films protect the copper matrix as long as they are not mechanically damaged. When the films are mechanically damaged, as they are in even mild forming operations, such as straightening sheet, involving less than 1 percent plastic deformation, they do not repair themselves spontaneously with protective copper oxide free films at normal temperatures or in the absence of special atmospheres.

Accordingly, it is an object of the present invention to provide a process for the preparation of new and improved copper base alloys which have substantial resistance to oxidation.

It is a further object of the present invention to provide new and improved copper base alloys which are ca-

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pable of substantial resistance to oxidation under a wide variety of conditions.

It is a still further object of the present invention to provide alloys as aforesaid, the oxidation resistance of which is not impaired when the alloy is mechanically damaged, i.e., it is an object of the present invention to provide ennobled, oxidation-resistant copper base alloys.

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

In accordance with the present invention it has now been found that the foregoing objects and advantages of the present invention may be readily accomplished and new and improved copper base alloys capable of substantial resistance to oxidation may be prepared. The novel alloys of the present invention may be prepared by (A) providing from 2.0 to 25.0 percent by weight of two elements, with the ratio of the first to the second of said elements being from 0.03:1 to 10:1, the first of said elements being selected from the group consisting of: aluminum; gallium; indium; and beryllium, the second of said elements being selected from the group consisting of: silicon; germanium; tin; and beryllium, provided that when beryllium is the second element, aluminum is the first element; (B) alloying said elements with copper; and (C) heating said alloy in an oxidizing environment for at least one minute at a temperature of from 400° C. to the solidus temperature of the alloy to form a first outside layer 25 to 5000 Angstroms in depth of copper oxides and oxides of said alloying additions and a second oxidation resistant layer immediately beneath said first layer containing a discrete dispersion of a complex oxide including at least one of said alloying additions, said second layer being of a thickness of at least 50 Angstroms and preferably substantially greater.

Under optimum conditions the first layer may be bright and shiny and oxidation resistant; however, when it is necessary to remove the first layer in order to provide brightness or to perform some mechanical operations, the second highly ennobled oxidation resistant layer remains affording considerable protection to the alloy.

Accordingly, the novel, highly oxidation resistant alloys of the present invention comprise: (A) from 2.0 to 25 percent by weight of two alloying additions and the balance essentially copper, with the ratio of the first to the second of said alloying additions being from 0.03:1 to 10:1, the first of said alloying additions being selected from the group consisting of: aluminum; gallium, indium; and beryllium, the second of said alloying additions being selected from the group consisting of: silicon; germanium; tin; and beryllium, provided that when beryllium is the second alloying addition aluminum is the first alloying addition; and (B) said alloy having an oxidation resistant zone of at least 50 Angstroms in depth containing a discrete dispersion of a complex oxide including at least one of said alloying additions.

In accordance with the present invention the improved properties of the alloys of the present invention are imparted primarily by the discrete dispersion of complex oxide including at least one of said alloying additions in a subsurface layer. These complex oxides are present in a metal matrix generally free from separated copper oxides and upon removal of the first outside layer provide a bright and shiny article having extensive resistance to oxidation, resistance to most aggressive chemical reagents and extensive resistance to further oxidation and tarnishing over a wide range of temperatures at or below the formation temperature of the oxidation resistant zone. In addition, in some cases the first outside layer is bright and shiny.

In addition to the foregoing, it is also surprising that the second layer containing the dispersed oxide is not brittle and does not suffer from grain boundary weak-

ness. It is a surprising feature of the present invention that the alloys containing this dispersed oxide layer are ductile and can be bent and formed by deep drawing.

The present invention is related in theory to copending application Ser. No. 281,992 by Michael J. Pryor, filed May 21, 1963, now U.S. Patent 3,259,491. In accordance with said copending application, an oxidation resistant copper base alloy is formed by bulk alloying with copper at least two alloying ingredients in concentration ratios to form certain complex oxides on the surface of the alloy, i.e., the alloying ingredients are added in concentration ratios so that they diffuse to the surface of the alloy in proportion to the concentration of the individual alloying ingredient in the complex oxide. The complex oxides formed in said copending application are similar to and in some instances the same as the complex oxides formed in the alloy of the present invention as a discrete dispersion in the oxidation resistant zone.

The above copending application provides an alloy representing a considerable advance in the art and affording a high degree of oxidation resistance. The alloys of said copending application are particularly advantageous at elevated temperatures and provide extensive oxidation resistance at, for example, 800° C. However, the disadvantage of the alloys of said copending application is that less protection is afforded over a wide range of temperatures, for example, from 0° C. to 550° C. Said copending application discloses modifications which achieve a greater degree of oxidation resistance over a wide temperature range, but the protection afforded while considerable still leaves room for improvement.

It is the particular advantage of the present invention that extensive oxidation resistance is achieved over a wide range of temperatures. This oxidation resistance is obtained by a simple and convenient process and with a surprisingly inexpensive alloy. The alloys and process of the present invention are especially surprising in view of the long and fruitless quest for a process which achieves an alloy of this type.

In accordance with the present invention a total of from 2 to 25 percent by weight of two elements are alloyed with copper. The amount from 2 to 25 percent is the total combined weight of both elements which are added. The first element is selected from the group consisting of aluminum, gallium, indium and beryllium and the second element is selected from the group consisting of silicon, germanium, tin and beryllium, provided that when beryllium is the second element aluminum must be the first element.

The total combined amount of the first and the second element is from 2 to 25 percent by weight and the preferred combined amount is from 2 to 7 percent by weight. The relative ratio of the first to the second of said elements must be maintained with the following ratio, from 0.03:1 to 10:1. That is, the ratio of the first to the second of said elements must be maintained within the foregoing ratio. Naturally, the ratio which is chosen for a particular system will vary widely within the foregoing broad ratio depending upon the particular system and the relative atomic weights of the elements which are added. For example, when the alloying additions are aluminum and silicon, which is preferred, the following ratio of aluminum to silicon should be employed, from 2.5:1 to 0.5:1. Similarly, for elements which have lower or higher atomic weights than aluminum, the ratio should be adjusted, for example, the beryllium-silicon system utilizes the following ratio of beryllium to silicon, 2.0:1 to 0.15:1. The indium-silicon system utilizes the following ratio of indium to silicon, 10:1 to 0.2:1. The gallium-silicon system utilizes the following ratio of gallium to silicon, 10:1 to 0.2:1. The aluminum-germanium system utilizes the following ratio of aluminum to germanium, 5:1 to 0.2:1 and the aluminum-tin system utilizes the following ratio of aluminum to tin, 3:1 to 0.03:1. Similarly, the following ratios apply to the following systems: aluminum

to beryllium, 10:1 to 0.5:1; gallium to germanium, 5:1 to 0.1:1; gallium to tin, 3:1 to 0.1:1; indium to germanium, 10:1 to 0.2:1; and indium to tin, 5.0:1 to 0.1:1.

It should be noted that the exact proportion of the first alloying addition to the second alloying addition will be affected by the atomic weights of the respective elements, the specific complex oxides desired to be formed, and also the diffusion and chemical characteristics of the particular alloying additions.

As indicated above, it is a requirement of the present invention that from 2 to 25 percent by weight of the two alloying additions are added to copper and alloyed therewith. Naturally, the present invention contemplates within its scope the use of other materials in combination with copper and the two metal alloying additions in order to achieve particularly desired results or to provide a particular alloy. For example, still greater oxidation resistance may be obtained by adding the following in addition to the two principal alloying ingredients: boron; manganese; zinc; and beryllium where beryllium is not one of the alloying ingredients. Also, particularly desired properties may be enhanced by the addition of other alloying ingredients while retaining oxidation resistance.

In accordance with the present invention, the particular method of alloying copper with the chosen alloying additions is not particularly important and conventional methods may be readily employed provided that the molten copper to which the alloying elements are added is initially oxygen free so that the alloying elements are not present in the alloy as oxides prior to solidification. As is conventional, the elements may be added as master alloys or in elemental form.

It is a critical aspect of the present invention, however, that after the alloying additions have been added to copper, the alloy solidified and if desired brought into a suitable or desired product form, the resultant alloy is heated in oxidizing environment for at least one minute, and preferably at least five minutes, at a temperature of from 400° C. to the solidus temperature of the alloy.

In the preferred embodiment, the alloy is heated in an oxidizing atmosphere, such as air, to desired temperatures at a rate of at least 5° C. per hour. Naturally, the particular temperature of treatment will vary depending upon the particular system and the particular results desired. However, in the preferred embodiment a temperature range of from 500° C. to 850° C. is employed, and optimally a still more preferred range of from 600° to 800° C. is used. The time of holding the alloy at these elevated temperatures should for practical purposes be less than 2 days, although longer heater times may be utilized if desired. The optimum heating time is from one (1) hour to 10 hours.

It is critical that the alloy be heated in an oxidizing environment. Any oxidizing environment may be readily employed, for example, preferably air or oxygen and also molten oxidizing salt baths may be employed, such as those containing sodium nitrate.

After the alloy has been held under the above conditions the alloy is preferably cooled to room temperature.

Under optimum treatment conditions, the foregoing process results in a surface which is bright and shiny. However, the outside surface is not the oxidation resistant zone but comprises a thin first zone, normally varying in thickness from 25 to 5000 Angstroms depending upon the time and temperature of treatment and the particular alloy utilized. The first zone may, however, provide some oxidation resistance and it is often desirable to retain the first zone. This first outside zone could be and often is mottled or darkened in appearance. The physical composition of this first or outside zone is a thin layer of copper oxides which may contain in addition, the oxides associated with one or both alloying additions either singly or in combination. For example, in an aluminum-silicon system, the first or outermost layer may contain alumina, silica and also complex oxides of aluminum and silicon.

A conventional pickling may be employed to remove any surface blemishes. The pickling step assists in providing a uniformly shiny and bright physical appearance by removing dark, discoloring, unsightly oxides which precede the formation of the more protective oxides during the oxidation heating. Naturally, the pickling procedure should not remove the second zone. Alternately, conventional metal removal techniques, such as mechanical buffing and polishing, etc., may be used.

Where the outside zone is bright and shiny in appearance, some oxidation protection may be afforded thereby. However, the principal oxidation protection afforded by the alloys of the present invention is provided by the zone immediately beneath the first zone. This oxidation resistant second zone provides the major advantages of the present invention.

It is preferred, although not necessarily essential, to remove the outside or first zone by any desired means in order to bare the second zone. That is, after the first zone is removed, the outermost zone is the second zone or oxidation resistant zone. The first zone may be removed by any desirable means, such as pickling or buffing or some mechanical forming operation.

The depth of the second zone will vary widely depending upon the particular treatment conditions, with in all cases the thickness being at least 50 Angstroms. In general, in order to provide reasonable oxidation protection, the second zone should be a minimum of 50 Angstroms in depth and preferably at least 200 Angstroms. The maximum depth of the second or oxidation resistant zone is completely dependent upon the treatment conditions and the particular system utilized, that is, longer holding times and higher temperatures will provide a thicker oxidation resistant zone. Normally, however, a second or oxidation resistant zone of around 2 mils is the preferred value, although for some uses it may be preferable to get a thicker oxidation resistant zone or even if desired obtain an oxidation resistant zone which comprises all of the rest of the alloy.

The oxidation resistant zone is characterized by containing a discrete dispersion of complex oxides including at least one of said alloying additions. The discrete dispersion is present in the metal matrix. The complex oxides are similar to and in some cases the same as the complex oxides in said copending patent application Ser. No. 281,992.

In accordance with the present invention the second or oxidation resistant zone is bright and shiny in appearance and provides the extensive oxidation resistance referred to hereinabove, that is, oxidation resistance over a wide temperature range at or below the formation temperature range. In other words, oxidation and tarnish resistance is provided in a bright and shiny alloy having characteristics desired in alloys of this type over a wide temperature range up to the temperature of the heat treatment step. This second or oxidation resistant zone behaves chemically as if it were a more noble metal than copper, i.e., it resists chemical attack by many strong chemical reagents which are normally used for pickling copper.

Beneath the oxidation resistant zone is normally the copper base alloy itself. This base would normally have only the original oxidation resistance in the absence of the oxidation resistant zone of the present invention, but would not have the enhanced resistance.

The second or oxidation resistant zone depends for its formation on the inward migration of oxygen. Therefore, some equilibrium solubility for oxygen in the base metal is required. Hence, the principle of the present invention may be extended to an alloy system which has significant solubility for oxygen, e.g., iron, silver, gold and zirconium, with of course copper being preferred. The present invention achieves an ennobling of the base alloy, i.e., makes the alloy behave as if it were a more noble metal.

In addition, the principle of the present invention may be extended to heating in anions other than oxygen, while

of course oxygen is preferred. Examples of such other anions are: fluorides; carbides; phosphides; sulfides; nitrides; and dispersions of intermetallics. Naturally, the base metal must have significant solubility for the particular anion.

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

EXAMPLE I

A copper base alloy was prepared utilizing high purity copper and high purity alloying additions. The alloy was prepared by tilt mold casting into a 1¾ x 1¾ x 4 inch shape, heating to 1600° F. (871° C.), hot rolling in a number of passes to 0.190 inch, and cold rolling and annealing into 10 mil sheet. The resultant alloy had a composition containing 3 percent aluminum and 2 percent silicon and the balance essentially copper.

EXAMPLE II

The alloy prepared in Example I, in 10 mil sheet, cold rolled form, was carefully cleaned and heated for two hours at various temperatures from 350° to 800° C. The weight gain in micrograms per square centimeter is shown in the graph which is the drawing of the present application. This weight gain represents the initial oxidation which results in the copper-aluminum-silicon alloy. After the heating at the temperatures of 350-600° C. the alloy was mottled and darkened in color, although at 800° C. it remained bright and shiny in color.

As a comparative example the same copper-aluminum-silicon alloy in the same form was cleaned and subjected to the treatment conditions of the present invention as follows: the specimen was first heated at 800° C. for 2 hours in air; followed by cooling to room temperature; followed by vigorously attacking for about 100 seconds with an etchant composition of 10 percent concentrated sulfuric acid, 40 percent concentrated nitric acid and 50 percent glacial acetic acid in order to remove about 800 micrograms per square centimeters, i.e., in order to remove the first or outside zone and to bare the second or oxidation resistant zone. The resultant specimen was bright and shiny in appearance.

The resultant specimen was then reoxidized for two hours in the temperature range between 350 and 800° C. The weight gain in micrograms per square centimeter may be seen in the drawing of the present application. In particular it should be noted that the weight gain was reduced to about one-third of that characteristic of the otherwise untreated base alloy. In the 350° C. temperature range, much larger reductions of oxidation rate of a factor of around one-twentieth are obtained. After the 2 hour oxidation treatment of the alloy of the present invention, the specimens remained bright and shiny at all temperatures in contrast to the darkened and mottled appearance of the copper-aluminum-silicon alloy when given the single initial heating at 350 to 600° C.

For comparison purposes, relative oxidation rates of conventional copper base alloys are shown in FIGURE 1. The alloys shown are: 70-30 brass; and a copper base alloy containing 10 percent nickel and 0.1 percent chromium.

EXAMPLE III

A copper-aluminum-beryllium alloy was prepared in the same manner as Example I to have a composition as follows: 1.74 percent aluminum; 0.34 percent beryllium; and the balance essentially copper.

The alloy thus prepared, in 10 mil sheet cold rolled form, was then carefully cleaned and heated in air at a temperature of 350° C. for 2 hours. The total weight gain after the 2 hour heating period was 38 micrograms per square centimeter and the sample was mottled in color.

A fresh sample of the same copper-aluminum-beryllium alloy in the same form was carefully cleaned and heated at a temperature of 800° C. for 2 hours open to the

air atmosphere. The sample was then cooled to room temperature and vigorously attacked with an etchant composition as in Example II in order to remove about 2300 micrograms per square centimeter, i.e., in order to remove the first or outside zone and etch into the subsurface metallic oxidation resistant zone. The sample was immersed in the etchant composition for a period of 20 seconds and was bright and shiny in appearance thereafter. The sample was then heated at 350° C. in air for a period of 2 hours. Following this treatment, the total weight gain of the sample in micrograms per square centimeter was less than the maximum sensitivity of the microbalance, i.e., the total was less than one (1) microgram. The sample of the alloy of the present invention remained bright and shiny after the above treatment.

EXAMPLE IV

An alloy was prepared in the same manner as Example I to have the following composition: silicon 1.25 percent; beryllium 0.8 percent; and the balance essentially copper.

The sample in the 10 mil sheet cold rolled form was cleaned and was heated at 350° C. in air for 2 hours. The weight gain after the 2 hour period was 46 micrograms per square centimeter and the sample was darkened and mottled in appearance.

A fresh sample of the same alloy in the same form was cleaned and heated in air at 800° C. for 2 hours. The sample was then cooled to room temperature and vigorously attacked with an etchant solution as in Example II for 160 seconds in order to remove about 13,000 micrograms per square centimeter resulting in a bright and shiny article. The sample was then heated at 350° C. in air for 2 hours and the weight gain was 21 micrograms per square centimeter. Following this reoxidation treatment the sample retained its bright and shiny appearance.

EXAMPLE V

An alloy was prepared in the same manner as Example I to have the following composition: gallium 2.47 percent; silicon 3.71 percent; and the balance essentially copper.

The alloy in the 10 mil sheet cold rolled form was carefully cleaned and heated in air at 350° C. for 2 hours. The sample showed a weight gain of 22 micrograms per square centimeter and had a slightly mottled appearance.

A fresh sample of the same alloy in the same form was cleaned and heated at 800° C. in air for 2 hours. The sample was then vigorously attacked with an etchant solution as in Example II for 160 seconds in order to remove about 9,000 micrograms per square centimeter, i.e., in order to remove the first zone and etch into the second oxidation resistant zone. The sample was bright and shiny in appearance after this treatment. The sample was then heated in air for 2 hours at 350° C. and showed a weight gain of 12 micrograms per square centimeter while retaining its bright and shiny appearance.

EXAMPLE VI

An alloy was prepared in the same manner as Example I to have a composition of 1.03 percent aluminum; 3.88 percent germanium; and the balance essentially copper.

The alloy in the 10 mil sheet cold rolled form was cleaned and heated at 350° C. for 2 hours in air. The thus heated sample showed a weight gain of 71 micrograms per square centimeter and was darkened and mottled in appearance.

A fresh sample of the same alloy in the same form was cleaned and heated for 2 hours open to the atmosphere at 800° C. The sample was then cooled to room temperature and vigorously etched as in Example II in order to remove about 1700 micrograms per square centimeter and to bare the second zone. The etching treatment was continued for 20 seconds and the resultant sample was bright and shiny in appearance. The sample was then heated at 350° C. in air for 2 hours which resulted in

a weight gain less than the maximum sensitivity of the microbalance, i.e., the total was less than one (1) microgram, with the sample still bright and shiny in appearance.

EXAMPLE VII

An alloy was prepared in the same manner as Example I to have a composition of 1.13 percent aluminum; 4.44 percent tin; and the balance essential copper.

The alloy in the 10 mil sheet cold rolled form was cleaned and heated at 350° C. for 2 hours in air. The thus heated sample showed a weight gain of 48 micrograms per square centimeter and was darkened and mottled in appearance.

A fresh sample of the same alloy in the same form was cleaned and heated for 2 hours open to the atmosphere at 800° C. the sample was then cooled to room temperature and vigorously etched as in Example II in order to remove about 4200 micrograms per square centimeter and to bare the second zone. The etching treatment was continued for 20 seconds and the resultant sample was bright and shiny in appearance. The sample was then heated at 350° C. in air for 2 hours which resulted in a weight gain of 22 micrograms per square centimeter while retaining its bright and shiny appearance.

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. A process for the preparation of a copper base alloy capable of substantial resistance to oxidation which comprises:

(A) providing from 2.0 to 25 percent by weight of two elements, with the ratio of the first to the second of said elements being from 0.03:1 to 10:1, the first of said elements being selected from the group consisting of: aluminum; gallium; indium; and beryllium, the second of said elements being selected from the group consisting of: silicon; germanium; tin; and beryllium, provided that when beryllium is the second element, aluminum is the first element;

(B) alloying said elements with copper;

(C) heating the resultant alloy in an oxidizing environment for at least one minute at a temperature of from 400° C. to the solidus temperature of the alloy to form a first outside layer 25 to 5000 Angstroms in depth of copper oxides and oxides of said alloying additions and a second oxidation resistant layer immediately beneath said first layer, said second oxidation resistant layer having a metal matrix containing a discrete dispersion of a complex oxide including at least one of said alloying additions, said second layer being of a thickness at least 50 Angstroms; and

(D) removing said first outside layer.

2. A process according to claim 1 wherein said first and second elements are aluminum and silicon respectively in a ratio of from 2.5:1 to 0.5:1.

3. A process according to claim 1 wherein said first and second elements are gallium and silicon respectively in a ratio of from 10:1 to 0.2:1.

4. A process according to claim 1 wherein said first and second elements are aluminum and germanium respectively in a ratio of from 5:1 to 0.2:1.

5. A process according to claim 1 wherein said first and second elements are indium and silicon respectively in a ratio of 10:1 to 0.2:1.

6. A process according to claim 1 wherein said first and second elements are beryllium and silicon respectively in a ratio of 2:1 to 0.15:1.

- 7. A process according to claim 1 wherein said first and second elements are aluminum and tin respectively in a ratio of 3:1 to 0.03:1.
- 8. A process according to claim 1 wherein said first and second elements are aluminum and beryllium respectively in a ratio of 10:1 to 0.5:1.
- 9. A process according to claim 1 wherein said first and second elements are gallium and germanium respectively in a ratio of 5.0:1 to 0.1:1.
- 10. A process according to claim 1 wherein said first and second elements are gallium and tin respectively in a ratio of 3:1 to 0.1:1.
- 11. A process according to claim 1 wherein said first and second elements are indium and germanium respectively in a ratio of 10:1 to 0.2:1.
- 12. A process according to claim 1 wherein said first and second elements are indium and tin respectively in a ratio of 5:1 to 0.1:1.
- 13. A process according to claim 1 wherein said alloy is heated in an oxidizing environment for from 5 minutes to 2 days at a temperature of from 500 to 850° C.
- 14. A process according to claim 1 wherein said alloy is heated at a rate of at least 5° C. per hour to a temperature of from 600 to 800° C. and held at that temperature in an oxidizing environment for from 1 hour to 10 hours.
- 15. A copper base alloy capable of substantial resistance to oxidation comprising:
 - (A) from 2.0 to 25 percent by weight of two alloying additions and the balance essentially copper, with the ratio of the first to the second of said alloying additions being from 0.03:1 to 10:1, the first of said alloying additions being selected from the group consisting of: aluminum; gallium; indium; and beryllium, the second of said alloying additions being selected from the group consisting of: silicon; germanium; tin; and beryllium, provided that when beryllium is the second alloying addition aluminum is the first alloying addition; and
 - (B) said alloy having an oxidation resistant zone of at least 50 Angstroms in depth, said oxidation resistant zone having a metal matrix containing a discrete dispersion of a complex oxide including at least one of said alloying additions.
- 16. An alloy according to claim 15 wherein said first

- and second alloying additions are aluminum and silicon respectively in a ratio of from 2.5:1 to 0.5:1.
- 17. An alloy according to claim 15 wherein said first and second alloying additions are beryllium and silicon respectively in a ratio of 2:1 to 0.15:1.
- 18. An alloy according to claim 15 wherein said first and second alloying additions are gallium and silicon respectively in a ratio of from 10:1 to 0.2:1.
- 19. An alloy according to claim 15 wherein said first and second alloying additions are aluminum and germanium respectively in a ratio of from 5:1 to 0.2:1.
- 20. An alloy according to claim 15 wherein said first and second alloying additions are indium and silicon respectively in a ratio of 10:1 to 0.2:1.
- 21. An alloy according to claim 15 wherein said first and second alloying additions are aluminum and tin respectively in a ratio of 3:1 to 0.03:1.
- 22. An alloy according to claim 15 wherein said first and second elements are aluminum and beryllium respectively in a ratio of 10:1 to 0.5:1.
- 23. An alloy according to claim 15 wherein said first and second elements are gallium and germanium respectively in a ratio of 5.0:1 to 0.1:1.
- 24. An alloy according to claim 15 wherein said first and second elements are gallium and tin respectively in a ratio of 3:1 to 0.1:1.
- 25. An alloy according to claim 15 wherein said first and second elements are indium and germanium respectively in a ratio of 10:1 to 0.2:1.
- 26. An alloy according to claim 15 wherein said first and second elements are indium and tin respectively in a ratio of 5:1 to 0.1:1.

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