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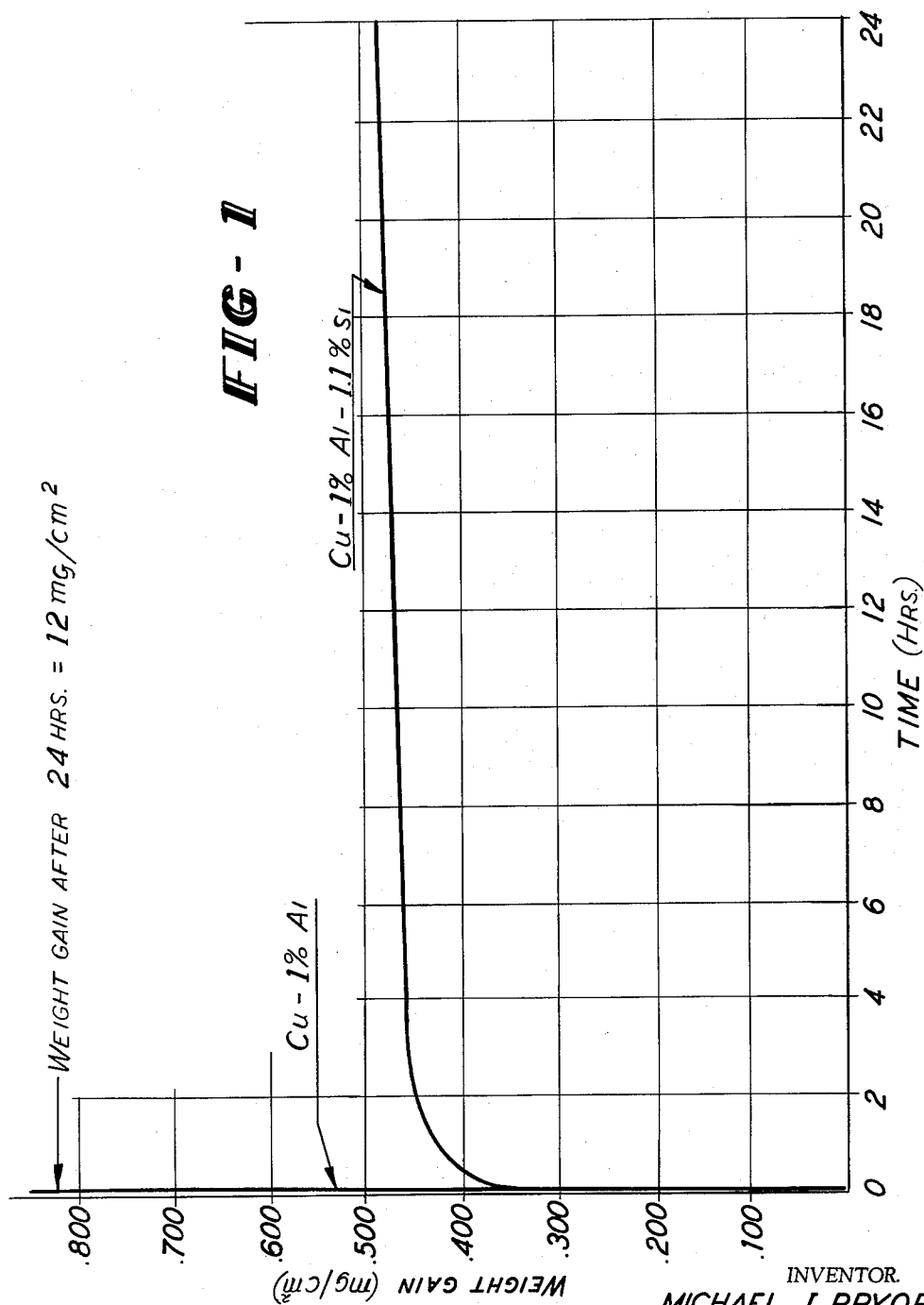
M. J. PRYOR

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COPPER BASE ALLOYS AND PROCESS FOR PREPARING SAME

Filed May 21, 1963

2 Sheets-Sheet 1



INVENTOR.

MICHAEL J. PRYOR

BY

Robert H. Boehmer

ATTORNEY

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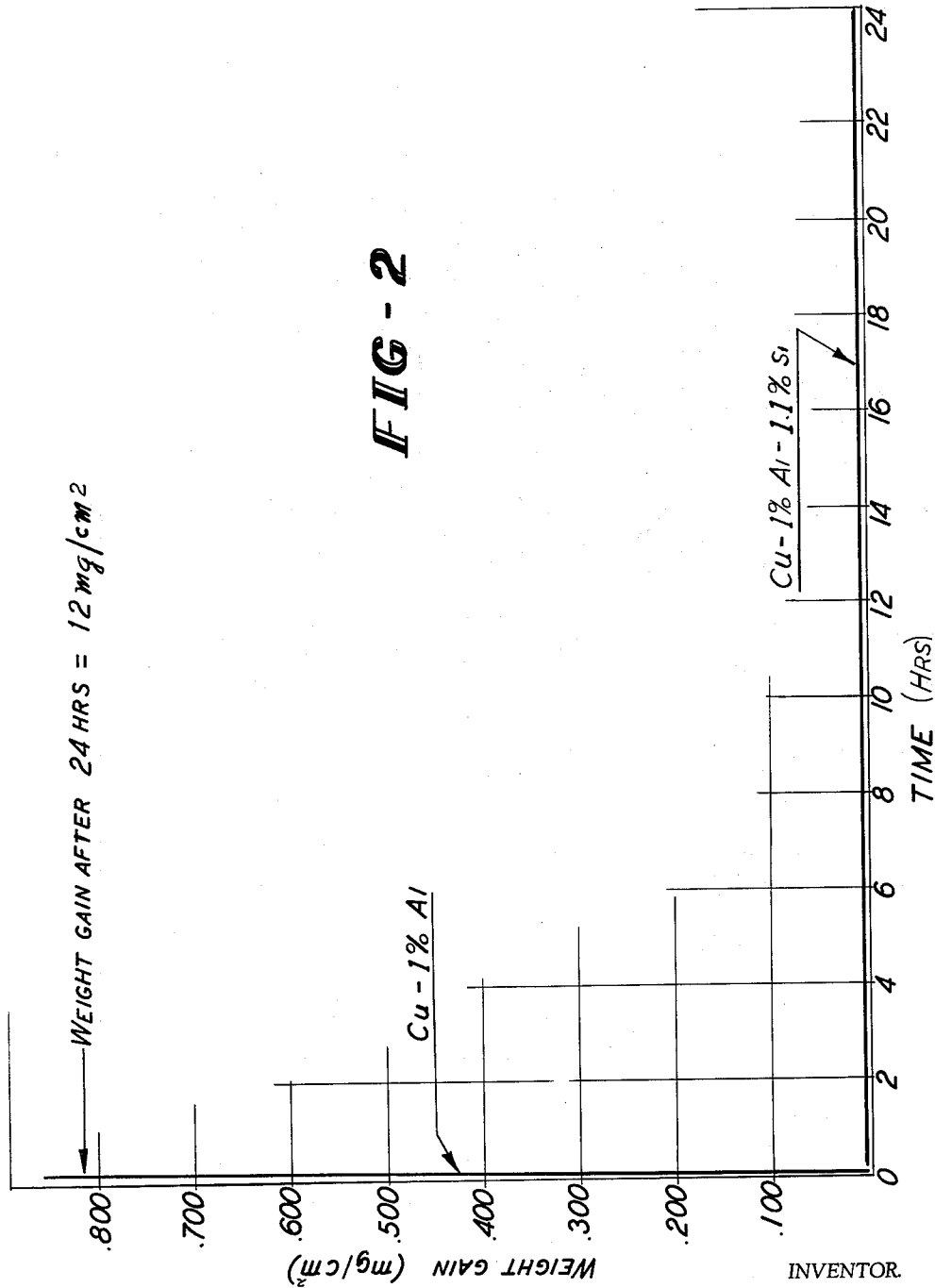
M. J. PRYOR

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INVENTOR.

MICHAEL J. PRYOR

BY

Robert H. Boesman

ATTORNEY

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COPPER BASE ALLOYS AND PROCESS FOR PREPARING SAME

Michael J. Pryor, Hamden, Conn., assignor to Olin Mathieson Chemical Corporation, a corporation of Virginia

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The present invention relates to new and improved copper base alloys having substantially improved resistance to oxidation and tarnishing in moist and contaminated atmospheres.

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 maintained the copper, with its lower free energy 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 capable 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 self-healing, oxidation-resistant copper base alloys.

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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 comprise a copper base alloy having on its surface a complex oxide formed from at least two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of greater than 0.5 percent by weight, said complex oxide having:

(A) A melting point above 1300° C., often incongruent;

(B) Less than 0.5 percent solid solubility by weight for copper oxides;

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide; and

(D) Preferably having a high electrical resistivity at room temperature, i.e., about 10^{10} ohm centimeters at room temperature.

The novel alloys of the present invention are readily prepared by bulk alloying the alloying ingredients in concentration ratios to form the 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.

Complex oxides having the foregoing characteristics are known. It is a surprising feature of the present invention that the alloying additions may be added in the appropriate concentration ratios and provide a highly oxidation resistant alloy.

The process of the present invention and the novel alloys obtained thereby, surprisingly and unexpectedly overcome the problems heretofore encountered in the extensive studies of the copper base alloy art. It is surprising and unexpected to find that a self-healing copper base alloy may be readily and expeditiously obtained, in view of the long and fruitless efforts to solve this problem. The alloys of the present invention are oxidation resistant when subjected to a wide variety of conditions, for example, the alloys of the present invention were found to be resistant to tarnishing when: heated in air in elevated temperatures on the order of 800° C. for long periods of time; when exposed to contaminated moist air for long periods of time; and even when immersed in corrosive solutions, such as ammonium sulfide solution. As is well known, conventional copper base alloys tarnish to a very high degree upon even short exposures under these conditions.

The alloying ingredients which are contemplated in the the present invention are metals having a maximum solid solubility in copper of greater than 0.5 percent by weight. In addition, the alloying ingredients are those which form the foregoing complex oxides on the surface of the copper base alloy when added in the appropriate combinations and concentrations. Naturally, the particular combination of alloying ingredients and the bulk alloying concentration ratios thereof will depend upon the particular complex oxide and the proportion of the individual alloying ingredients therein.

Representative alloying ingredients include, but are not limited to, aluminum, silicon, gallium, chromium, titanium, beryllium, zirconium, boron, magnesium, nickel, germanium, manganese and iron.

In accordance with the information at hand it is believed that when the alloying ingredients are added in the appropriate concentration ratios the surface of the

alloy contains the complex oxide as aforesaid; however, the exact mechanism of the present invention is not fully understood, and therefore, the critical aspect of the present invention is the addition of the alloying ingredients in an amount calculated to form on the surface the foregoing complex oxides.

Exemplificative complex oxides contemplated in accordance with the present invention include some of those of the spinel group. Complex oxides may be formed from two or more alloying additions, with the alloying additions in each case being added in the concentration ratio required to form the particular complex oxide, i.e., where, for example, a three-component complex oxide exists the alloying ingredients are added in proportion to the concentration of the individual alloying ingredients in the complex oxide. In Table I below there is listed representative series of alloying additions and complex oxides, contemplated in the present invention.

Table I.—Alloying ingredients

Alloying Ingredients	Complex Oxide System and Formula(s)	Compound Melting Point ° C.	Maximum Solid Solubility for Either Oxide Component	Interfacial Atomic Concentration Ratio
Beryllium and Aluminum	Beryllium Aluminates: 3Al ₂ O ₃ ·BeO	1,910	Nil	6Al:1Be.
Aluminum and Silicon	Al ₂ O ₃ ·BeO	1,870	Nil	2Al:1Be.
Beryllium and Silicon	Mullite, 3Al ₂ O ₃ ·2SiO ₂	1,810	Nil	3Al:1Si.
Magnesium and Boron	Beryllium Silicate, 2BeO·SiO ₂	1,560	Nil	2Be:1Si.
	Magnesium Borate: 2MgO·B ₂ O ₃	1,356	Nil	1Mg:1B.
Magnesium and Silicon	3MgO·B ₂ O ₃	1,340	Nil	3Mg:2B.
Magnesium and Titanium	Forsterite, 2MgO·SiO ₂	1,890	Nil	2Mg:1Si.
	Magnesium Titanate: 2MgO·TiO ₂	1,732	Nil	2Mg:1Ti.
	MgO·TiO ₂	1,630	Nil	1Mg:1Ti.
	MgO·2TiO ₂	1,652	Nil	1Mg:2Ti.
Aluminum and Titanium	Aluminum Titanate, Al ₂ O ₃ ·TiO ₂	1,860	Nil	2Al:1Ti.
Zirconium and Silicon	Zirconium Silicate, ZrSiO ₄	1,540	Nil	1Zr:1Si.
Beryllium and Chromium	Beryllium Chromite, BeO·Cr ₂ O ₃	>1,500	Nil	1Be:2Cr.
Zirconium and Titanium	Zirconium Titanate, ZrO ₂ ·TiO ₂	1,600	Nil	1Zr:1Ti.

In accordance with the present invention the bulk concentration ratios are adjusted on the basis of standard diffusion theory so that the two or more alloying ingredients arrive at the alloy surface by diffusion in the appropriate atomic concentration to form the stoichiometric complex oxide. The appropriate amounts of the alloying ingredients can be simply calculated in accordance with standard diffusion theory, that is, standard diffusion theory enables us to determine the bulk alloying composition at any given temperature to fulfill the appropriate interfacial atomic concentration ratios listed in Table I. For a discussion of standard diffusion theory, see "Atom Movements" by L. S. Darken in American Society for Metals, 1951. Naturally, for example, an alloy "diffusion balanced" for 800° C. will not be "diffusion balanced" for 500° C.; however, in accordance with the present invention alloys may be obtained which are oxidation resistant over a wide range of temperatures by increasing the bulk alloy concentration. Generally, as the total bulk alloy concentration is increased a greater flexibility and temperature tolerance is obtained. Accordingly, with more highly alloyed copper compositions containing at least two principal alloying additions, high oxidation resistance is obtained over a wide temperature range.

The alloying ingredients are added in the appropriate concentration ratios, as indicated hereinabove, with a variation of ± 10 percent from the calculated concentration ratio being tolerable. This gives oxidation resistance over the limited temperature range for which the concentration ratios are calculated. If the ± 10 percent tolerance is exceeded, no significant benefit is obtained. However, it is a further and especially surprising feature of the present invention that this ± 10 percent limit may be exceeded when the alloying additions are added in an amount of at least 50 percent of the combined maximum solubility of the alloying additions in the alpha phase

field at the appropriate diffusion balanced temperature. In fact, in this situation an excess may be desirable in order to provide a "doping" effect, discussed hereinafter, which provides even further improved oxidation resistance over a wider temperature range.

In accordance with the present invention additional improvement may be obtained by including in the alloy, in addition to the ingredients discussed heretofore, at least 0.1 percent of an element which generates a cation having a valence state of at least two and which has a maximum solid solubility in copper of greater than 0.5 percent by weight.

The additional improvement obtained by the inclusion of the above additional element is due to the "doping" effect which the additional element has on the cuprous oxide present on the surface of the alloy. The surface of the improved alloy of the present invention contains a proportion of cuprous oxide, the amount of which de-

pends on many factors, including the particular alloying ingredients, amounts thereof, temperature, etc. Cuprous oxide is a non-protective oxide having low electrical resistance and containing substantial concentrations of cupric ions substituted in the cuprous ion cation lattice. The cuprous oxide exhibits a very low ionic resistance due to the existence of a substantial number of cation vacancies, directly proportional to the concentration of cupric ions, and also exhibits a low electronic resistance resulting from the ease of electron exchange between cuprous and cupric ions.

Accordingly, the present invention also provides that residual copper oxides on the surface can be rendered more protective by bulk alloying the complex copper alloy of the present invention with an additional element as aforesaid. This additional element, which is a higher valency cation than cuprous ions, becomes included in the cation lattice of the residual oxides of copper in replacement for the strongly reducing cupric ions and causes a "doping" effect which results in extremely high electronic resistivity.

The additional or "doping" element should be added in an amount of at least 0.1 percent and preferably less than 5.0 percent, with the most effective proportion of each particular element depending upon, for example, the particular element added and the particular alloy and composition thereof.

The additional or doping element, in addition to the requirements hereinabove mentioned, should preferably be of a strongly reducing nature, i.e., the free energy of formation of its natural oxide should be at least 25 percent higher than cuprous oxide. Also, the doping element should easily enter the cation lattice of cuprous or cupric oxide and have no adverse interaction effects with the other alloying components. Naturally, more than one of such additional elements may be added.

Representative "doping" elements include, but are not

limited to, the following, or mixtures thereof: aluminum; silicon; gallium; zinc; nickel; manganese; beryllium; chromium; titanium and zirconium.

This additional element can be provided by adding an excess of at least one of the two alloying ingredients forming the complex oxide provided that the alloying additions are added in an amount of at least 50 percent of the combined maximum solubility of the alloying additions in the alpha phase field at the appropriate diffusion balanced temperature and provided, of course, that the requirements of a "doping" element are met. Alternatively, a suitable additional element can be used, as discussed heretofore. The additional element should preferably exhibit only a single valency state so that electron exchange between the substituted ion in the residual cu-

percentages are weight percentages unless indicated otherwise.

EXAMPLES 1 AND 2

Two experimental alloys were prepared containing small amounts of binary and ternary alloying additions which produce the appropriate interfacial conditions for the complex oxide systems, mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and beryllium aluminate, $\text{Al}_2\text{O}_3 \cdot \text{BeO}$. These alloys were prepared with a bulk concentration of 1 percent by weight of aluminum and with calculated amounts of silicon and beryllium being added to satisfy interfacial surface atom ratios outlined in Table I at a temperature of 800° C. The actual bulk compositions of these "diffusion balanced" alloys are contained in Table II.

Table II

Example No.	Percent, Cu	Percent, Al	Percent of Third Element	Complex Oxide System
1-----	97.82	.99	1.12% silicon-----	Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.
2-----	98.79	1.06	.094% beryllium-----	Beryllium Aluminate, $\text{Al}_2\text{O}_3 \cdot \text{BeO}$.

prous oxide and cuprous oxide will be prohibitively high and therefore, greatly restrict, if not prevent completely, the normal easy electron exchange between cuprous and cupric ions in the cuprous oxide. Multivalent elements may be used as the additional ingredients provided that one valency state is substantially more stable than the rest.

A still further improvement is obtained by the addition of a rapidly diffusing alloying addition, i.e., at least 0.02 percent by weight, and preferably, between 0.02 and 0.3 percent by weight, of an element having an interfacial dilution ratio greater than 0.02.

The interfacial dilution ratio of an element *x* can be readily calculated in accordance with the following equation:

$$\text{Interfacial dilution ratio} = [\text{Cx}][\text{Dx}] / [\text{CCu}][\text{DCu}]$$

wherein Cx and CCu are the atomic concentrations of the elements *x* and copper, respectively; wherein Dx is the single diffusion coefficient of element *x* at an atomic concentration of Cx and at the appropriate temperature; and wherein DCu is the self diffusion coefficient of copper at the same temperature.

This additional element is characterized by rapidly diffusing to the surface of the alloy so that it dilutes the copper concentration at the alloy-atmosphere interface. The rapidly diffusing element serves to reduce the amount of copper oxide that must be doped to maintain the highly protective nature of the overall multiphase film.

Additional preferred attributes of the rapidly diffusing elements are that they should exhibit a high degree of solid solubility in copper, should not interact adversely with the diffusion characteristics of the other diffusion balancing and doping alloying additions, should form either an unstable oxide or a stable oxide which is more protective than suitably doped cuprous oxide, and should not form low resistance compounds with the complex, compound oxide.

For example, suitable rapidly diffusing diluent alloying additions to stainless copper compositions include nickel, aluminum, beryllium, manganese and mixtures thereof.

The neutral, rapidly diffusing diluent alloying additions effectively reduce the interfacial concentration of copper and therefore the amount of suitably doped cuprous oxide formed in the surface film, thereby assisting the development of premium, self-healing stainless behavior.

It should be realized that, while copper is preferred, the principle of the present invention is applicable to other matrix metals than copper, such as silver, nickel, aluminum and zirconium.

The present invention and the improvements attained thereby will be more readily apparent from a consideration of the following illustrative examples, wherein all

EXAMPLE 3

The alloys prepared in Examples 1 and 2 were heated in air for two hours at 800° C. The total weight gains due to oxidation after this treatment were compared with those of copper and a copper-one percent aluminum alloy. The results are contained in Table III and show that the alloys of Examples 1 and 2 exhibit substantially lower oxidation rates than copper or copper-aluminum alloy.

Table III

Alloy:	Weight gain mg./sq. cm.
Copper-----	4.4
Copper-1% aluminum-----	2.5
Alloy of Example 2-----	2.1
Alloy of Example 1-----	0.5

It is evident that both alloys of Examples 1 and 2 reduce the oxidation rate, but that the alloy of Example 1 is more effective.

EXAMPLE 4

The comparison between the alloy of the present invention and the copper-one percent aluminum alloy control is even more graphic in the continuous weight gain time curves shown in FIGURE 1. These tests, obtained with a continuous recording microbalance, show the continuous gain in weight, with time upon heating various copper-aluminum base alloys in oxygen at a pressure of 76 mm. of mercury. When the copper-one percent aluminum control and the "diffusion balanced" copper-aluminum-silicon alloy of Example 1 were heated at 800° C., the copper-aluminum alloy showed an extremely high weight gain after a very short period of time, and a total weight gain of 12 milligrams after 24 hours. The alloy of Example 1, however, oxidized only for a short period of around 30 minutes and thereafter showed little or no weight gain for periods as long as 24 hours. The slope of the weight gain vs. time curve for this complex alloy is essentially flat between these two times indicating the development of an unusually protective film for any known copper alloy.

EXAMPLE 5

Example 4 was repeated, with the exception that the alloys tested, i.e., the alloy of Example 1 and the copper-one percent aluminum alloy, were heated to 800° C. in vacuum and the same oxidizing atmosphere admitted (oxygen at 76 mm. of mercury). The results are shown in the continuous weight gain time curves of FIGURE 2. These results show essentially no weight gain of the alloy of Example 1 after 24 hours. Furthermore, the alloy remained in the same bright and golden condition after the 24 hour period, i.e., the alloy was truly stainless. In

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comparison, the copper-aluminum alloy showed substantially the same behavior as in Example 4.

Examples 6 and 7, which follow, show the use of aluminum as a doping additive, wherein the alloying ingredients, silicon and aluminum, are added in an amount of at least 50% of their combined maximum solubility in the alpha phase field.

EXAMPLE 6

In a manner after Examples 1 and 2 a "diffusion balanced" copper-aluminum-silicon alloy was prepared, diffusion balanced for 800° C., having the following composition:

	Percent
Aluminum -----	1.75
Silicon -----	2.14
Copper, essentially the balance.	

Oxidation tests were performed on two samples of this alloy in laboratory air containing normal industrial contaminants by slowly heating each sample from room temperature to 600 and 800° C., respectively, followed by a soak period of two hours at 600 and 800° C., respectively, and air cooling to room temperature. After these extreme treatments the alloy exhibited an extremely high degree of stainless performance over the entire temperature range. The alloy was not substantially tarnished, showing only occasional patches of light interference colors. The sample treated at 800° C. showed a total weight gain of 0.067 milligram/sq. cm. The sample given the treatment at 600° C. showed a total weight gain of 0.044 milligram/sq. cm.

As a comparison, austenitic stainless steel was subjected to the same test conditions and a substantially greater tarnishing effect was clearly evident.

EXAMPLE 7

In a manner after Examples 1 and 2 a copper-aluminum-silicon alloy was prepared containing an excess of the aluminum alloying ingredient and having the following composition:

	Percent
Aluminum -----	3.14
Silicon -----	2.05
Copper, essentially the balance.	

Oxidation tests were performed on the samples of this alloy as in Example 6. After these extreme treatments the alloy exhibited an extremely high degree of stainless performance over the entire temperature range, slightly better than the alloy of Example 6. The sample given the treatment at 600° C. showed a total weight gain of 0.006 milligram/sq. cm. The sample given the treatment at 800° C. showed a total weight gain of 0.067 milligram/sq. cm.

EXAMPLE 8

In a manner after Examples 1 and 2 a "diffusion balanced" copper-aluminum-beryllium alloy was prepared, "diffusion balanced" for 800° C., having the following composition:

	Percent
Aluminum -----	1.74
Beryllium -----	0.34
Copper, essentially the balance.	

Oxidation tests were performed on two samples of this alloy as in Example 6. After these extreme treatments the alloy exhibited a high degree of stainless performance over the entire temperature range. The sample given the treatment at 600° C. showed a total weight gain of 0.140 milligram/sq. cm. The sample given the treatment at 800° C. showed a total weight gain of 0.346 milligram/sq. cm.

EXAMPLE 9

This example is comparative and shows that a "diffusion balanced" copper-aluminum-magnesium alloy



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does not exhibit the stainless behavior of the present invention since magnesium aluminate spinel shows extensive solid solubility for aluminum oxide.

Thus, in a manner after Examples 1 and 2 a "diffusion balanced," for 800° C., copper-aluminum-magnesium alloy was prepared having the following composition:

	Percent
Aluminum -----	1.91
Magnesium -----	0.80
Copper, essentially the balance.	

Oxidation tests were performed on two samples of this alloy as in Example 6. After these treatments the alloy showed weight gains of 0.309 milligram/sq. cm. for the 600° C. treatment and 0.480 milligram/sq. cm. for the 800° C. treatment.

EXAMPLE 10

As a further comparison, two samples of a copper-aluminum alloy containing 1.77 percent aluminum was subjected to the same treatment as in Example 6 and was severely blackened and tarnished, showing weight gains of 0.400 milligram/sq. cm. at the 600° C. treatment and 2.00 milligrams/sq. cm. at the 800° C. treatment.

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 copper base alloy capable of substantial resistance to oxidation consisting essentially of a copper base alloy having on its surface a complex oxide of at least two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of greater than 0.5 percent by weight, said complex oxide having:

- (A) A melting point above 1300° C.;
- (B) Less than 0.5 percent solid solubility by weight for copper oxides; and
- (C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide.

2. A copper base alloy capable of substantial resistance to oxidation consisting essentially of a copper base alloy having on its surface a complex oxide of two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of greater than 0.5 percent by weight, said complex oxide having:

- (A) A melting point above 1300° C.;
- (B) Less than 0.5 percent solid solubility by weight for copper oxides; and
- (C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide.

3. A copper base alloy according to claim 2 wherein said alloying additions are aluminum and silicon and wherein said complex oxide is mullite having the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

4. A copper base alloy according to claim 2 wherein said alloying ingredients are aluminum and beryllium and wherein said complex oxide is beryllium aluminate having the formula $\text{Al}_2\text{O}_3 \cdot \text{BeO}$.

5. A copper base alloy capable of substantial resistance to oxidation consisting essentially of a copper base alloy having on its surface a complex oxide of two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of greater than 0.5 percent by weight, said complex oxide having:

- (A) A melting point above 1300° C.;
- (B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide;

and containing at least 0.1 percent by weight of an element which generates a cation having a valence state of at least two and which has a maximum solid solubility in copper of greater than 0.5 percent by weight.

6. A copper base alloy according to claim 5 wherein said element is present in an amount between 0.1 and 5 percent by weight.

7. A copper base alloy according to claim 5 wherein said element is one of the alloying additions and wherein said alloying additions are present in an amount of at least 50 percent of the combined maximum solubility of the alloying additions in the alpha phase field.

8. A copper base alloy according to claim 7 wherein said alloying additions are aluminum and silicon, wherein said complex oxide is mullite, and wherein said element is aluminum.

9. A copper base alloy capable of substantial resistance to oxidation consisting essentially of a copper base alloy having on its surface a complex oxide of two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of greater than 0.5 percent by weight, said complex oxide having:

(A) A melting point above 1300° C.;

(B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide;

and containing at least 0.1 percent by weight of an element which generates a cation having a valence state of at least two and which has a maximum solid solubility in copper of greater than 0.5 percent by weight, and containing at least 0.02 percent by weight of an element having an interfacial dilution ratio of greater than 0.02.

10. A copper base alloy according to claim 9 wherein said element having an interfacial dilution ratio of greater than 0.02 is present in an amount of from 0.02 to 0.3.

11. A process for the preparation of a copper base alloy capable of substantial resistance to oxidation which comprises bulk alloying with copper at least two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of at least 0.5 percent by weight, said alloying additions being capable of forming a complex oxide having the following characteristics:

(A) A melting point above 1300° C.;

(B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide,

said alloying additions being added in concentration ratios so that they form said complex oxide on the surface of the alloy.

12. A process for the preparation of a copper base alloy capable of substantial resistance to oxidation which comprises bulk alloying with copper two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of at least 0.5 percent by weight, said alloying additions being capable of forming a complex oxide having the following characteristics:

(A) A melting point above 1300° C.;

(B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide,

said alloying additions being added in concentration ratios to diffuse to the surface of the alloy in proportion to their concentration in the complex oxide, thereby forming said complex oxide on the surface of the alloy.

13. A process according to claim 12 wherein said al-

loying additions are aluminum and silicon and wherein said complex oxide is mullite having the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

14. A process according to claim 12 wherein said alloying ingredients are aluminum and beryllium and wherein said complex oxide is beryllium aluminate having the formula $\text{Al}_2\text{O}_3 \cdot \text{BeO}$.

15. A process for the preparation of a copper base alloy capable of substantial resistance to oxidation which comprises bulk alloying with copper two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of at least 0.5 percent by weight, said alloying additions being capable of forming a complex oxide having the following characteristics:

(A) A melting point above 1300° C.;

(B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide,

said alloying additions being added in concentration ratios so that they form said complex oxide on the surface of the alloy and adding at least 0.1 percent by weight of an element which generates a cation having a valence state of at least two and which has a maximum solid solubility in copper of greater than 0.5 percent by weight.

16. A process according to claim 15 wherein said element is one of the alloying additions and wherein said alloying additions are bulk alloyed in an amount of at least 50 percent of the combined maximum solubility of the alloying additions in the alpha phase field.

17. A process according to claim 16 wherein said alloying additions are aluminum and silicon, wherein said complex oxide is mullite, and wherein said element is aluminum.

18. A process for the preparation of a copper base alloy capable of substantial resistance to oxidation which comprises bulk alloying with copper two metal alloying additions, each of said alloying additions having a maximum solid solubility in copper of at least 0.5 percent by weight, said alloying additions being capable of forming a complex oxide having the following characteristics:

(A) A melting point have 1300° C.;

(B) Less than 0.5 percent solid solubility by weight for copper oxides; and

(C) Less than 2 percent solid solubility by weight for the individual oxide components of the complex oxide,

said alloying additions being added in concentration ratios so that they form said complex oxide on the surface of the alloy and adding at least 0.1 percent by weight of an element which generates a cation having a valence state of at least two and which has a maximum solid solubility in copper of greater than 0.5 percent by weight and adding at least 0.02 percent by weight of an element having an interfacial dilution ratio of greater than 0.02.

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