United States Patent [19]

Ford et al.

[11] **3,728,155**

[45] **Apr. 17, 1973**

[54] **COPPER ALLOY CLEANING PROCESS**

[75] Inventors: **James A. Ford,** North Haven, Conn.; **Stuart R. Saunders,** Kingston, England; **Elmer J. Caule,** New Haven, Conn.; **Charles D. McLain,** Alton, Ill.

[73] Assignee: **Olin Corporation,** New Haven, Conn.

[22] Filed: **June 18, 1971**

[21] Appl. No.: **154,669**

Related U.S. Application Data

[62] Division of Ser. No. 789,417, Jan. 6, 1969, Pat. No. 3,646,946.

[52] **U.S. Cl.** **134/3,** 134/27, 134/28, 134/29, 134/30, 134/41

[51] **Int. Cl.** **C23g 1/04,** C23g 1/10, C23g 1/20

[58] **Field of Search**.....134/2, 3, 26–30, 134/41

[56] **References Cited**

UNITED STATES PATENTS

947,067	1/1910	Thompson	134/28
2,125,458	8/1938	Ostermann	134/3
2,284,743	6/1942	Kawecki et al.	134/29 UX
2,318,559	5/1943	Percival	134/3 UX
2,395,694	2/1946	Spence et al.	134/2 UX
2,726,970	12/1955	Toth	134/3
3,003,896	10/1961	Kendall	134/3
3,121,026	2/1964	Bergay et al.	134/2

Primary Examiner—Barry S. Richman

Attorney—Paul Weinstein et al.

[57] **ABSTRACT**

A process for removing surface oxides from copper alloys. For example, those alloys which form, on annealing, Al_2O_3 and related oxides are uniquely cleaned by a process which consists of a duplex treatment requiring a first immersion in a hot alkaline solution followed by a second immersion in a hot mineral acid solution.

10 Claims, No Drawings

COPPER ALLOY CLEANING PROCESS

This application is a division of application Ser. No. 789,417, filed Jan. 6, 1969, no U.S. Pat. No. 3,646,946.

Many copper base alloys, especially those containing aluminum, form complex thermal oxides which are difficult to remove by conventional copper cleaning techniques.

For example, a copper alloy containing about 66 percent copper, 1.55 percent aluminum, 1.0 percent iron, balance essentially zinc, forms a refractory thermal oxide during annealing that cannot be reliably removed using ordinary cleaning procedure. The metal cannot be reproducibly soldered or electroplated because of the residual annealing oxide.

In addition to causing soldering and plating problems, excessive residual Al_2O_3 can cause excessive die wear and failure during fabrication operations.

It is the object of the present invention to achieve easy and reproducible removal of these films.

It is another object of the present invention to remove those films within the confines of existing copper-base alloy cleaning equipment.

Other objects and advantages will become apparent from the following description.

In accordance with the present invention the foregoing objects are readily obtained. The process of the present invention comprises: immersing the surface to be cleaned in an aqueous alkaline solution having a pH above 10 for at least 2 seconds, with the solution being at a temperature of from 100°F to the boiling point; and then immersing the surface to be cleaned in an aqueous mineral acid solution at a temperature of from 75°F to 200°F for from 2 seconds to 5 minutes, said solution having an acid equivalent to an H_2SO_4 solution of 3 to 50 percent by volume. Preferably, a conventional water rinse or air wipe is performed between steps and after the final step.

The exact time and the exact bath temperature in each of these two steps is determined by the type of annealing operation and the character of the resulting oxide including its thickness and constitution.

The process is suitable to both continuous cleaning of strip and to batch cleaning of fabricated parts.

Following the described cleaning process, copper base alloys coated with complex oxides can be successfully soldered and electroplated because the residual oxide resulting from annealing has been removed.

The process of the present invention is effective for any copper base alloy. The present process is especially effective with copper alloys containing as alloying additions: aluminum, from 0.5 to 12 percent; and silicon, from 0.5 to 5 percent. The process of the present invention is particularly useful with respect to copper alloys bearing: complex oxides; alumina; spinel type oxides, such as copper aluminate and zinc aluminate; nickel oxides; etc.

As indicated hereinabove, the process of the present invention utilizes a duplex treatment requiring a first immersion in a hot alkaline solution followed by a second immersion in a hot mineral acid solution.

Concerning the first alkaline solution, any alkaline solution may be used which has a pH above 10 and preferably a pH from 11 to 14. Preferred solutions which may be used depend, of course, upon the particular alloy and the results desired. In general, caustic

soda is the preferred alkaline solution, but others may be readily employed such a lithium or potassium hydroxide, for example. The alkaline solution should be maintained at a temperature of from 100°F to the boiling point, and preferably at a temperature of from 160°F to the boiling point. The copper alloy to be cleaned should be immersed in the solution for at least 2 seconds and preferably for from 5 seconds to 1 minute. Naturally, longer treatment times may be employed, but in general no advantage is obtained thereby. Generally, the treatment time should be under 10 minutes. Naturally, temperature and time are related and the exact treatment conditions are dependent upon the alloy used and the results desired.

The second immersion in acid may employ any mineral acid solution having an acid equivalent to an H_2SO_4 solution of 3 to 50 percent by volume. In general, any mineral acid may be used with sulfuric acid being preferred. Others which may be used include nitric and hydrochloric, for example. The preferred solution has an acid equivalent to an H_2SO_4 solution of from 5 to 20 percent by volume. The mineral acid solution should be maintained at a temperature of from 75°F to 200°F and preferably at a temperature of from 125°F to 175°F. A treatment time of at least 2 seconds should be employed and preferably from 5 seconds to 1 minute. The mineral acid treatment should generally not exceed 5 minutes as in some cases there is obtained an undesirable blush color for treatment times in excess of about 5 minutes. The alloy is, of course, effectively cleaned; however, the color is undesirable commercially.

Naturally, both the first and second solutions should be aqueous solutions.

Preferably, a conventional water rinse or air wipe is preferred between the steps and after the final step.

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

EXAMPLE I

In this example, the following alloys were processed.

TABLE I

Alloy	Composition
A	Aluminum, 9.5%; Iron, 3.8%; Copper, essentially balance
B	Aluminum, 2.8%; Silicon, 1.8%; Cobalt, 0.4%; Phosphorus, 0.1%; Copper, essentially balance
C	Zinc, 22.7%; Aluminum, 3.4%; Cobalt, 0.4%; Copper, essentially balance

The alloys were processed as shown in Table II, below, which shows bath concentration and residence times and temperatures for air, bell, and strip annealing oxides for each alloy.

Air annealing was carried out as follows: The alloy sheet was brought to a temperature of about 1,100°F in several minutes and held at that temperature for 2 hours. The alloy was then cooled to room temperature by removal from the furnace. Air had access to the interior of the furnace.

Bell annealing refers to annealing in which sheet material was placed in a closed furnace. Air was displaced with an atmosphere resulting from hydrocarbon combustion. The furnace was brought to a temperature

of about 1,100°F over a period of several hours. The furnace was held at temperature for a period of several hours, after which it was slowly cooled over several hours to a temperature at which the furnace could be opened without promoting excessive oxidation.

In strip annealing, a strip is continuously fed through a furnace heated, for example, by gas burners or resistance heat and continuously exits therefrom with a gas atmosphere in the furnace produced by burning propane to eliminate oxygen. The rate of travel is adjusted so that residence time in the furnace is sufficiently long that the strip reaches the desired temperature, 1,100°F, in this case.

TABLE II

Alloy A	Alloy B	Alloy C
Treatment Following Air Anneal		
NaOH — pH 11 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each — 30 sec.	NaOH — pH 11 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 30 sec.	LiOH — pH 12 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 30 sec.
Treatment Following Bell Anneal		
NaOH — pH 13 Temp — Boiling pt. H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 15 sec.	NaOH — pH 14 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 15 sec.	NaOH — pH 14 Temp — Boiling pt H_2SO_4 — 12% vol % +4 oz/gal Sodium Dichromate—150°F Time in each— 15 sec.
Treatment Following Strip Anneal		
NaOH — pH 14 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 5 sec.	NaOH — pH 14 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 5 sec.	NaOH — pH 14 Temp — Boiling pt H_2SO_4 — 12% vol % Temp. — 150°F Time in each— 5 sec.

It should be noted that the alkaline immersion for air annealed alloy C for short treatment times should use lithium hydroxide. In addition, an acid bath composition modification was used for the bell annealed alloy C treatment. In this latter case, sodium dichromate should be added to the acid bath in the range of from 1 to 8 ounces per gallon in order that the last 25 Angstroms of Al_2O_3 might be removed.

This acid dichromate bath modification can be used with the other alloys; however, it produces an etched surface which appears hazy or frosty; an undesirable surface condition for the final product. This is not important in most instances since further cold rolling and strip annealing will produce a bright surface.

It was found that after the cleaning process described above, all alloys were successfully soldered after cleaning. By comparison, prior to cleaning, none of these alloys could be soldered.

EXAMPLE II

The efficacy of the foregoing cleaning procedure has been accurately demonstrated by utilizing surface capacitative measurements before and after cleaning. It has been found that the cleaning technique described effectively increases the surface capacitance, a parameter linked to the thermal oxide thickness and solution double layer thickness, to a value indicative of only the surface double layer capacitance produced by immersion of the test specimen in the electrolytic solution used in capacity measurement. For example, a specimen of alloy C before cleaning was covered by a film of oxide which capacitance measurements allowed to be calculated 88 Angstroms thick. After cleaning, the thickness of oxide and double layer equivalent was 4.8 Angstroms. Correction for the double layer reduces any total value less than 8 Angstroms to zero thickness of oxide. Effectively, the capacitance bridge showed that the surface was cleaned. This was confirmed by the solder test.

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 cleaning a copper base alloy surface having a thermally formed oxide thereon, said alloy containing aluminum and said oxide containing at least in part aluminum oxide, comprising: immersing the surface to be cleaned in an aqueous alkaline solution having a pH of from 10 to 14 at a temperature from 160°F to the boiling point of said aqueous alkaline solution for a period of time of at least 2 seconds; and then immersing the surface to be cleaned in an aqueous mineral acid solution at a temperature of from 75°F to 200°F for from 2 seconds to 5 minutes, said acid solution having an acid equivalent to an H_2SO_4 solution of 3 to 50 percent by volume.

2. A process according to claim **1** in which sodium dichromate is present in the acid solution in an amount of from 1 to 8 ounces per gallon.

3. A process according to claim **1** in which the oxide is at least in part a spinel.

4. A process according to claim **1** in which said alkaline solution contains lithium hydroxide.

5. A process according to claim **1** in which said alkaline solution contains sodium hydroxide.

6. A process according to claim **1** in which the acid solution consists essentially of an aqueous solution of H_2SO_4.

7. A process according to claim **1** in which the thickness of the oxide after cleaning is less than 10 Angstrom.

8. A process according to claim **1** wherein the temperature of said alkaline solution is at the boiling point.

9. A process according to claim **1** in which the temperature of the acid is from 125°F to 175°F.

10. A process according to claim **9** wherein said pH is from 11 to 14.

* * * * *