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METHOD FOR OXIDIZING ALLOYS
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6 Claims

ABSTRACT OF THE DISCLOSURE

A process for oxidizing alloys by first grit blasting and cleaning and then oxidizing the alloy at a temperature of 2000° F. to 2300° F. for 2 to 8 minutes to produce an oxide surface on said alloy.

The present invention pertains to a process for oxidizing alloys, and more particularly, the instant invention relates to a novel method for the oxidation of steel alloys to effect on said alloys a suitable surface for bonding to diverse interfaces. Specifically, the invention is directed to oxidizing steel alloys having surfaces adapted for metal-to-glass sealing.

Alloys, especially alloys consisting essentially of chromium-iron and chromium-nickel-iron, are widely used, because of their specific linear thermal coefficient of expansion, in devices for electronic use. For example, electron discharge tubes such as cathode-ray picture tubes for television reception employ alloys as anode buttons and studs. An anode button which is essentially a lead-in conductor element comprised of chromium-iron alloy or the like is sealed into the funnel wall with interior and exterior surfaces exposed for conduction of an electrical potential from conductively-coated interior surfaces of the completed tube to external electrical power sources. Studs or lugs made of chromium-iron alloys and like binary alloys are normally positioned within the glass in the skirt or flange portion of the tube face plate extending interiorly for positively retaining an extensive color shadow mask or line grid positioned in precise alignment with a luminescent target or screen on the tube viewing area.

To produce a good seal, it is very important for the metal alloys to have good sealing surfaces to obtain a strong bond between the alloy anode or stud and the glass part to which the alloy stud or anode is sealed. In the prior art attempts have been made to furnish a uniform layer of metal oxide over the sealing surfaces of the alloy or stud parts to increase the bonding of the glass-to-metal surfaces. The metal oxide layer of alloy preferably possesses properties of being both soluble in the glass and simultaneously firmly adhering to the base metal of the anode or stud part.

In order to obtain a metal oxide layer on the surface of a given alloy, the prior art generally employed hydrogen, usually a wet hydrogen atmosphere at elevated temperatures; but, considerable difficulty has been experienced in obtaining the necessary uniformity of the chromium-containing oxide film having satisfactory glass sealing properties. Also, the prior art wet hydrogen techniques often resulted in the objectionable formation of undesirable and uncontrollable flaky oxide films of varying thickness over the surface of the alloy parts. Other heretofore costly efforts involved special gaseous atmospheres coupled with highly select temperature conditions

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that required long treatment times and elaborate equipment.

It will be appreciated by those versed in the present art that if a novel and economical method is made available for the oxidization of alloys said method would represent an important contribution to the art. It will be further appreciated by those skilled in the present art that if a novel and unobvious method is made available that substantially eliminates the disadvantages intimately associated with the prior art, said method would have a positive economic value and also be an advancement in the fields of commerce and science.

Accordingly, it is a purpose of the present invention to provide a novel and unobvious method for oxidizing alloys under desirable conditions of time, temperature and atmosphere that will produce parts acceptable for use in the electronic industry.

Another purpose of the present invention is to provide an acceptable method for oxidizing the surfaces of alloys into a stable uniform oxide film having properties to permit glass-to-metal sealing in electronic tube parts and the like.

Still another purpose of the present invention is to provide an improved oxidized alloy stud or anode button for intimate sealing into television picture tube faceplates or funnels.

Yet a further purpose of the present invention is to provide an improved process for oxidizing alloy-type metals wherein said process does not require artificial atmosphere conditions.

Yet a still further purpose of the present invention is to provide an intimate oxide surface on an alloy part that is essentially free of entrapped gas bubbles and is essentially non-flaky.

In attaining the purposes, advantages and other features of the present invention, it has now been surprisingly found that an intimate, firmly bound oxide coat or layer can be produced on the exterior, exposed surfaces of alloys by subjecting said alloy to a process consisting of the steps of grit blasting, cleaning, degreasing, and air oxidation. More specifically, the novel process or method of the invention consists of grit blasting the alloy parts for a time sufficient to increase the exposed surface area thereof, usually about 10 to 40 minutes, cleaning the just grit-blasted alloy part by ultrasonic agitation in an organic cleaning-type solvent, usually at a temperature of about 150° F. to 190° F. in a trichloroethylene bath, air drying the clean degreased part, and then air oxidizing the alloy at a temperature ranging from about 2000° F. to 2300° F. for about 2 to 8 minutes to produce an oxide layer on said alloy part.

The alloys suitable for the purpose of the present invention are the commercially available alloys generally of the chromium-iron binary system. Usually, the concentration of the chrome is from 18 to 28% and the concentration of the iron is from 72 to 82%. Exemplary of a typical alloy used for the manufacture of anode and stud parts is the commercially available alloy known in the art as No. 430 alloy. Composition No. 430 contains 18% chromium and 82% iron. The binary also has traces of titanium, carbon, magnesium, phosphorus and silica. The thermal expansion coefficient of this type of alloy is approximately 115 to 120×10^{-7} cm./cm./degree through a range of 20° to 600° C. Another commercially-available alloy is the alloy designated as No. 446. A

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chemical analyses of No. 446 stainless steel alloy indicates that the alloy contains about 27–29% Cr, 0.12% C, 0.50–0.80% Mn, 0.20–0.80% Mg, 0.03% P, 0.03%–0.50% Ni, 0.10–0.15% N₂ and the balance Fe, with a coefficient of thermal expansion of $14 \times 10^{-7}/^{\circ}\text{C}$. (20°–600° C.). The presently listed alloys are merely representative of alloys suitable for the purposes of the present invention, and the invention is not to be construed as limited thereto as other suitable and functionally equivalent alloys will be self-apparent to those knowledgeable in the present art.

Exemplary of commercially-available organic solvents that can be used to clean the surfaces of the alloy are iso-butyl chloride, trichloroethylene, dioxolane, carbon tetrachloride, n-butyl chloride, benzene, cyclohexane and the like.

The reagents suitable for grit blasting for the purpose of this invention generally include the commercially-available siliceous materials, such as white rouge, silica in the form of quartz, tridymite or cristobalite, sand, mixtures such as white rouge and sand, and like grit blasting reagents.

The above-listed alloys generally match the expansion coefficient of the following glass which is conventionally employed for making television glass parts and they are particularly well-suited for sealing thereto. Exemplary of such glass, employed for fabricating faceplates and funnels, is one containing 58.9% SiO₂, 10.3% PbO; 4.2% Al₂O₃; 5.8% CaO; 2.1% MgO; 1.2% BaO; 7.7% Na₂O and 9.2% K₂O; and a glass consisting of 63.5% SiO₂; 4.4% Al₂O₃; 10.3% K₂O; 7.3% Na₂O; 5.2% CaO+MgO; 7.5% BaO, along with other minor constituents which are conventionally utilized to further control glass properties.

The following examples are set forth as representative methods illustrative of the spirit of the present invention. These examples are not to be construed as limiting the scope of the invention as other functionally equivalent means will be readily apparent to those skilled in the subject art.

EXAMPLE I

The exposed surfaces of commercially-available television studs were first grit blasted in a conventional laboratory grit blasting machine with 120 grit sand for 30 minutes. Next, the grit blasted studs were cleaned and degreased in a trichloroethylene ultrasonic agitation bath at a temperature of about 160° F. for 5 minutes, and then air dried with a conventional air gun. The clean studs were next placed in an electric heated furnace at a temperature of about 2100° F. for 6 minutes to produce the desired intimately-bound oxide coating on the exterior exposed surfaces of the studs.

EXAMPLE II

A group of studs were prepared as follows: first, the studs were grit sand blasted for 40 minutes, then they were transferred to a cleaning bath containing trichloroethylene. The studs were agitated in the bath at a temperature of about 160° F. for 5 minutes and then air dried with manual agitation. Next, the studs were oxidized at about 2100° F. for 6 minutes in an air atmosphere. The studs prepared in this manner were weighed before and after the oxidization step and they evidenced an increase in weight of about 1.4 mg. per stud as a result of the oxidization process.

EXAMPLE III

The process set forth in Example II was repeated for the present run, and, all conditions were as described supra, except that the studs were oxidized at about 2200° F. for 6 minutes. The studs showed an increase in weight of about 2.7 mg. per stud.

EXAMPLE IV

The process set forth in Example II was repeated for the present example, and all conditions were as set forth above, except that the studs were grit blasted for 20 minutes, than cleaned and finally air treated to produce an exterior oxide

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coating on the studs. The studs increased in weight about 2.1 mg. per stud.

EXAMPLE V

A group of chromium-iron alloy studs were chemical etched in 10% nitric acid bath for 10 minutes at 170° F. and then rinsed in distilled water. Next, the studs were forced air dried and then transferred to an electric furnace previously heated to 2100° F. The studs were permitted to air oxidize in the furnace for four minutes. Visual inspection of the studs evidenced a very good oxide coating on the exterior stud surface.

EXAMPLE VI

A No. 430 alloy stud was sand blasted for 30 minutes and then air oxidized at 2100° F. for about 6 minutes to produce an oxide layer on the stud. Next, a section of commercially available television glass, 1 inch by 1 inch by $\frac{3}{4}$ inch, was preheated with a gas-oxygen flame and the just oxidized No. 430 stud was preheated to 2000° to 2100° F. for 15 seconds with an RF generator. The piece of hot glass was forced onto the stud with both RF and flame heating, and after sealing, the glass-to-metal seal was flame annealed. Next, the television glass was mechanically shocked to remove the glass from the stud. The oxide layer remained on the stud, which indicates a good intimately-bound oxide layer on the stud.

EXAMPLE VII

A No. 430 alloy stud was sand blasted for 30 minutes with grit sand and then washed in an ultrasonic trichloroethylene bath for 5 minutes. Next, the exposed surfaces of the stud was oxidized in an air atmosphere at about 2200° F. for 6 minutes. The oxidized stud was next sealed into a piece of commercially-available glass consisting of 56.3 weight percent SiO₂, 1.9 weight percent Al₂O₃, 8.9 weight percent K₂O, 3.5 weight percent Na₂O and 29.1 weight percent PbO with RF heat, at a temperature of about 2200° F. to 2400° F. for 20 seconds. A close examination of the glass-to-metal seal did not evidence any trapped gas bubbles at or near the sealed surface.

The above examples are seen to demonstrate the unobvious and unexpected results produced by the process of the present invention. If studs are sand blasted for 5 or 10 minutes the oxide coating formed at 2100° F. for 6 minutes is generally poor and subject to stripping, while studs sand blasted for 20 to 40 minutes and oxidized at 2100° F. for 6 minutes have a very good oxide coating and resist stripping in the glass-to-metal seal. Also, studs oxidized at 2000° F. to 2200° F. for 3 to 8 minutes exhibited a good oxide surface with good adherence and a good tendency to resist reboil when sealed into glass during the glass-to-metal sealing process, while studs treated at a lesser temperature were prone to reboil.

The process of the present invention can be used to oxidize anode buttons and studs comprised of chromium-iron alloys that are used in the production of cathode-ray picture tube envelopes for television reception or in the manufacture of electron discharge tubes as conventionally employed in science and commerce.

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various modifications will be apparent and can readily be made by those skilled in the art without departing from the scope and spirit of the invention.

We claim:

1. An improved method of oxidizing the exposed surfaces of alloys selected from the group consisting of chromium-iron and chromium-nickel-iron alloys wherein said method consists essentially of the steps of grit blasting the exposed alloy surfaces, cleaning the grit-blasted surfaces with an organic solvent, and wherein the improvement comprises subjecting said clean alloy surfaces to an air atmosphere at a temperature ranging from about 2000° F. to 2300° F. about 2 to 8 minutes to effect an intimately bound oxide layer on said alloy.

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2. The method according to claim 1 wherein said alloy is grit-blasted for 10 to 40 minutes with a grit-blasting agent selected from the group consisting essentially of white rouge, sand, quartz, tridymite, cristobalite and mixtures thereof.

3. The method according to claim 1 wherein said organic solvent is trichloroethylene. 5

4. The method according to claim 1 wherein said alloy consists essentially of 18% chromium and 82% iron with traces of titanium, carbon, magnesium, phosphorus and silica. 10

5. The method according to claim 1 wherein said alloy consists essentially of 27-29% Cr, 71 to 73% iron with traces of carbon, magnesium, nickel and manganese.

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6. The method according to claim 1 wherein said air temperature is about 2100° F. for 6 minutes.

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