

April 19, 1960

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2,933,423

PREOXIDATION OF STAINLESS STEEL FOR GLASS-TO-METAL SEALING

Filed March 3, 1958

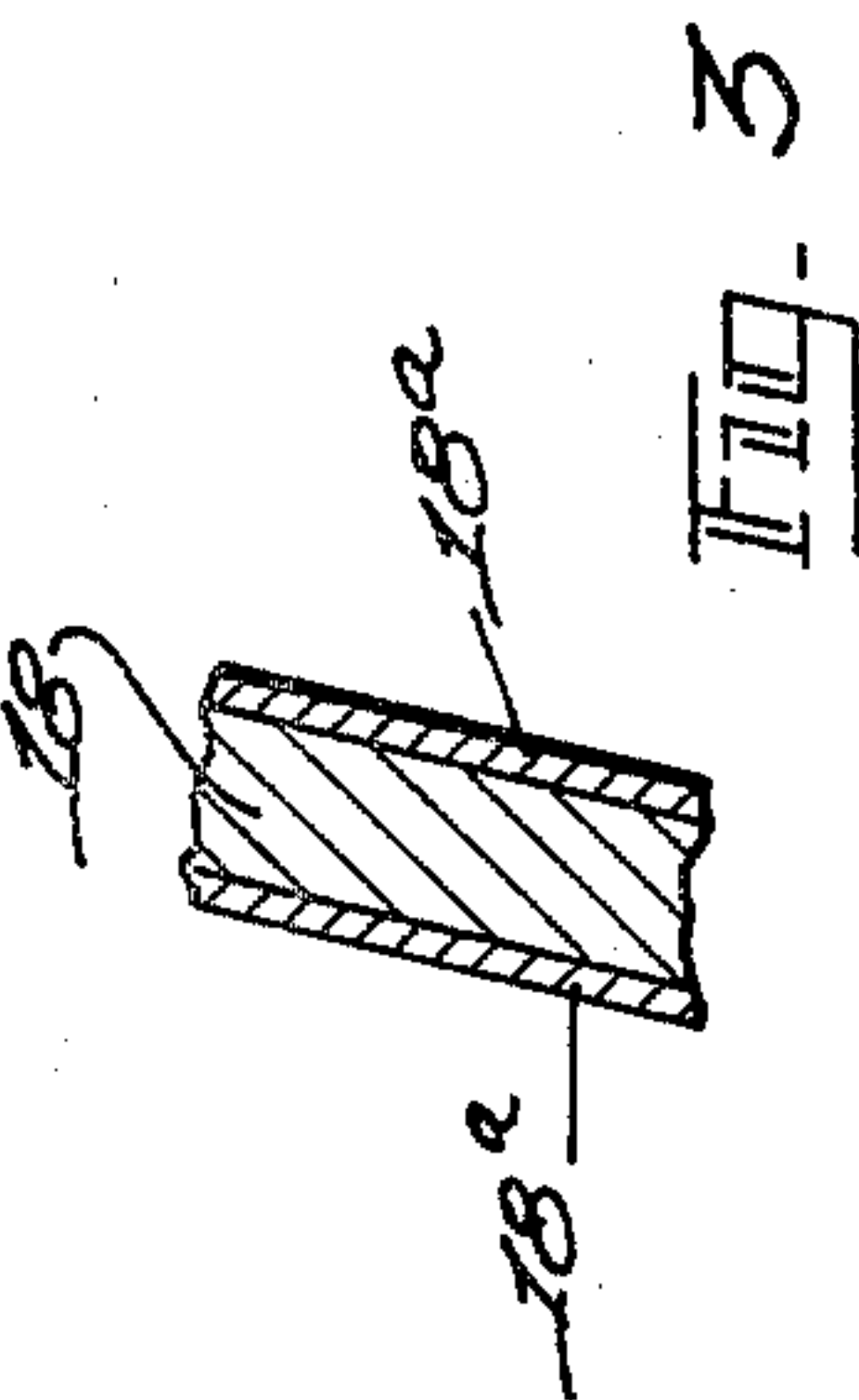
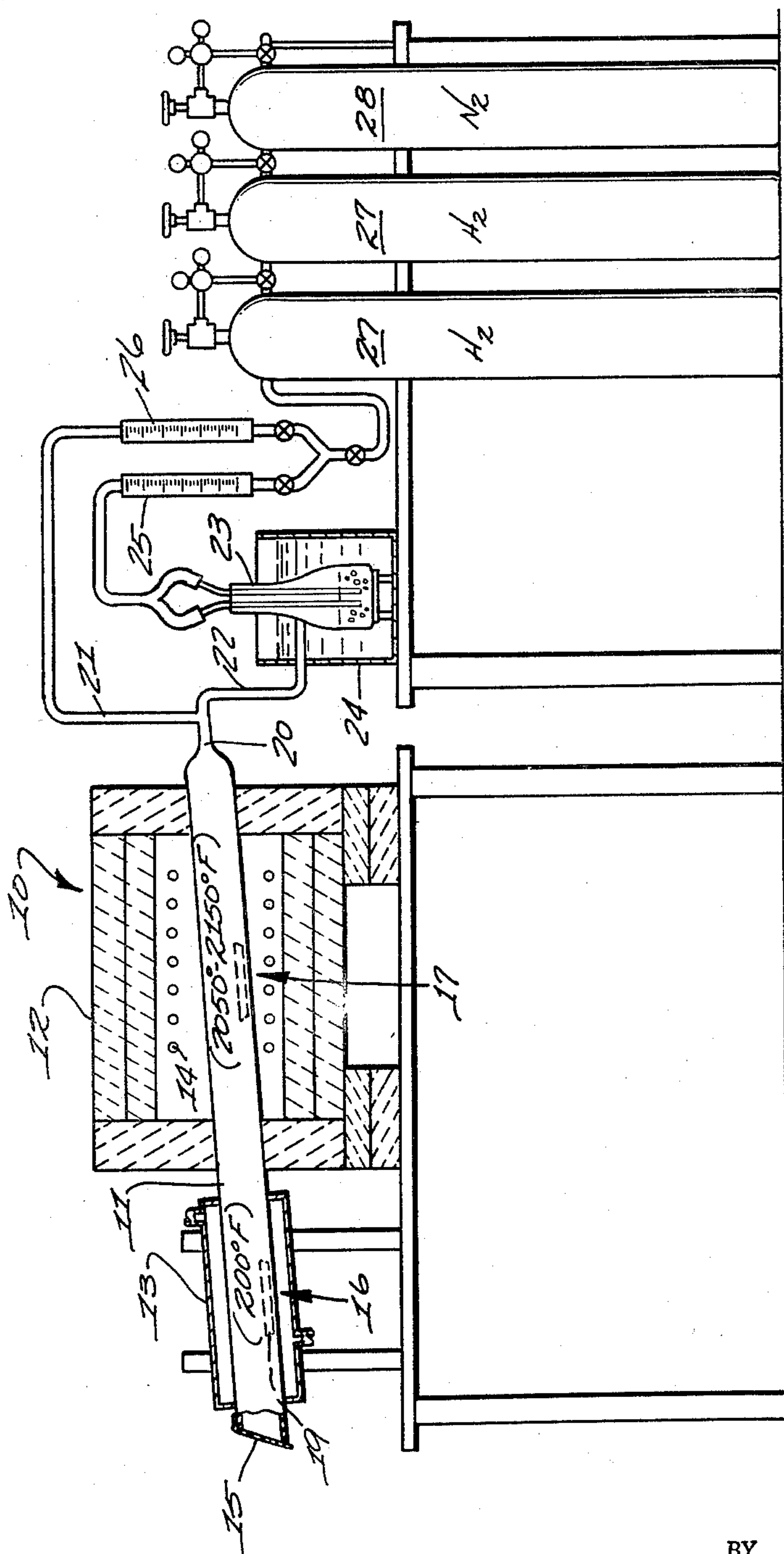


FIG. 1

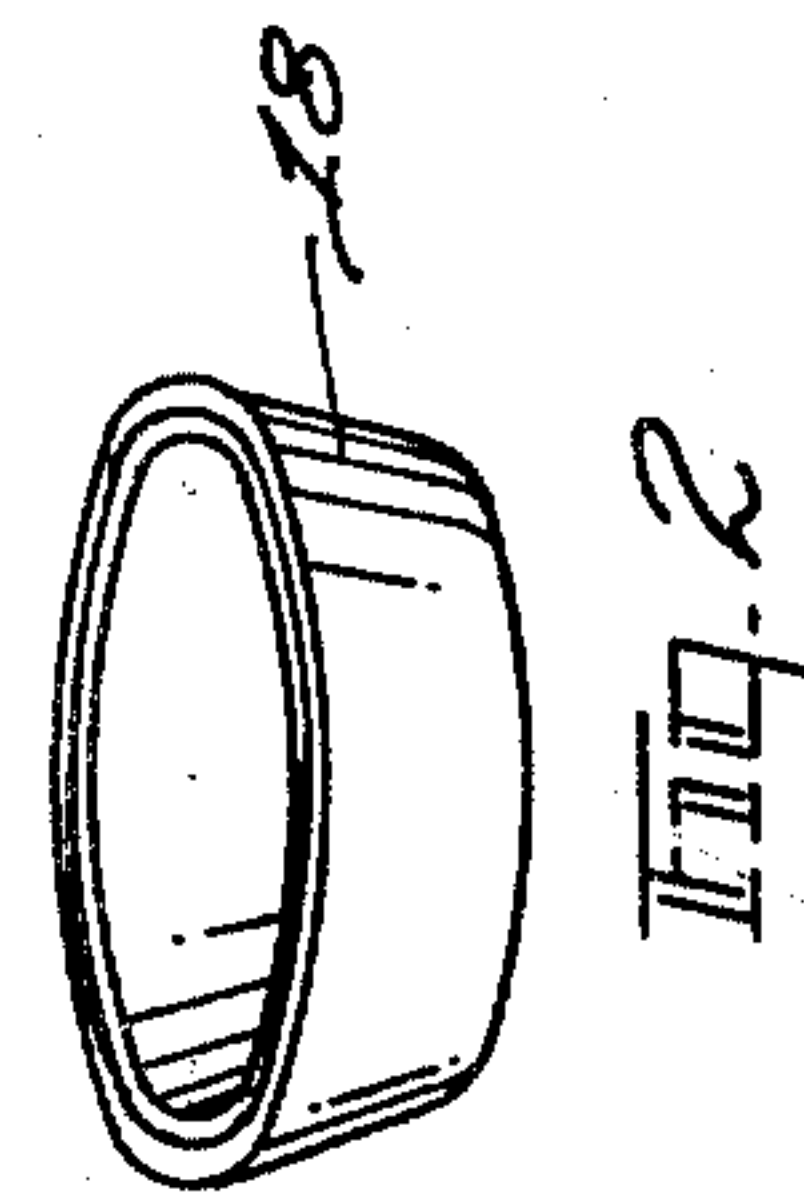


FIG. 2

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## PREOXIDATION OF STAINLESS STEEL FOR GLASS-TO-METAL SEALING

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Application March 3, 1958, Serial No. 718,566

5 Claims. (Cl. 148—6.35)

The present invention relates to stainless steel alloys having surfaces adapted to metal-to-glass sealing and more specifically to an improved process of preoxidizing the surfaces of certain stainless steel parts as a preliminary measure to creating improved durable and vacuum-tight metal-to-glass seals, the preoxidized surfaces forming the bonding interface therebetween.

As has been known heretofore, certain chromium-iron and chromium-nickel-iron alloys have been particularly well adapted, due to their specific thermal expansion coefficients, to sealing to a considerably wide range of glasses in manufacturing devices for electronic use. The sealing stresses created in the composite body, made by sealing a particular metallic part comprised of one of the aforementioned alloys sealed to glass, have been minimized by thermal expansion coefficients being properly matched and/or deviations therebetween being maintained in proper agreement.

In order to obtain a strong uniform bond between the metal and the glass to which the metal part is sealed, it has been required to furnish a relatively uniform layer of metal oxide over the sealing surfaces of the alloy parts. The oxide layer of alloy preferably possesses properties of being both soluble in the glass at or near the sealing temperatures and firmly adherent to the base metal of the part. An oxide layer can be obtained on the surface of chromium-bearing alloy parts by exposure to a stream of wet hydrogen while the parts are maintained at an elevated temperature, but considerable difficulty has been experienced in obtaining the necessary uniformity of the chromium containing oxide film having satisfactory glass sealing properties.

One process for oxidizing chrome-nickel-iron alloys for sealing to glass has been described in the patent to Kingston, Patent No. 2,502,855, issued April 4, 1950, entitled "Preoxidation of Stainless Steel." While this patent has taught a process of establishing the chromium oxide layer over the described alloy parts by subjecting the parts to a high velocity stream of wet hydrogen gas at a constant level of water content and at an elevated temperature of about 2300° F., objectionable formation of uncontrollably flaky oxide films of varying thickness frequently occurs over the surfaces of the preoxidized parts. Furthermore, the process is not considered applicable to preoxidation of chrome-iron alloy parts, for example, to achieve satisfactory results.

In the mass production of electron discharge tubes such as cathode-ray picture tubes for television reception, for example, it is essential that all metal-to-glass seals be as near perfectly vacuum-tight and as mechanically durable as possible in view of employment of the component parts in relatively high-speed sealing operations. In the production of glass funnels as one component part of cathode-ray picture tube envelopes, for example, a lead-in conductor element such as an anode button comprised of chromium-iron alloys is normally sealed into the funnel side wall with interior and exterior surfaces exposed for conduction of an electrical potential from conductively-

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coated interior surfaces of the completed tube to external sources. Another example of parts which may be sealed into such tube envelopes are mounting studs or lugs which are positioned within the glass in the skirt or flange portion of the tube face plate extending interiorly for positively retaining an extensive color-controlling element such as a shadow mask or line grid in precise alignment with a luminescent target or screen on the tube viewing area.

Obviously, it is exceedingly important that the surface of these metal alloy parts to be sealed to glass have surface layers which do not contain various oxides which tend to flake away from the base metal. As can be readily appreciated such flaking or separation from the base metal can be a direct cause of air leakage and tube failure due to separation of the metal surface and the oxide layer of the finished seal. It has been found that by employment of the subject method, metal alloy parts may be prepared having oxide coatings which facilitate their sealing to glass in an improved manner, as shown by stripping tests which measure the strength of resultant seals.

Also the parts may comprise lead-in conductors such as contact prongs which are mounted directly into a tube socket. It is necessary that the oxide film on the surfaces of the prongs or anode buttons not adhered to glass be adapted to removal as desired to furnish good electrical contact between the aforesaid lead-in conductors and socket contacts. Also, the surface oxide must be sufficiently removable from the surfaces of the parts where not sealed to glass to facilitate their welding to other tube elements whereby the part maintains its requisite electrical conductivity.

Accordingly, it is an object of the present invention to provide an improved method of preoxidizing the surface of stainless steel alloy parts under controlled conditions of time, temperature and atmosphere, the oxidized parts adapted to be sealed to electronic glasses in a vacuum-tight manner in variegated independent operations.

Another object of this invention is to provide an improved method of preoxidizing chromium-iron alloy parts under controlled conditions to provide a uniform adherent chromium oxide film over the exterior surfaces of the parts to permit their subsequent positive and non-stripable sealing to glass in hermetic and/or durable seals.

Another object of this invention is to provide a method of preoxidizing the surfaces of chrome-iron alloy parts into a stable uniform oxide film having properties to permit improved, structurally superior glass-to-metal sealing of electronic tube envelopes.

Another object of the present invention is to provide the unique method of preoxidizing chromium steel parts as a preliminary step prior to their being sealed to glass in vacuum-tight relationship wherein the oxide layer is exceedingly adherent and uniform, the parts being subjected to a controlled stream of wet hydrogen gas at both low and elevated temperatures, the degree of water vapor present being adjustably regulated during the preoxidation.

A still further object of the present invention is to provide a process of preoxidizing chrome-iron alloy shaped parts as a preliminary step to their being effectively sealed to glass, the preoxidation establishing a stable uniform oxide film over the exposed surfaces of the parts by subjection of the parts to both low and high temperatures while contained within a wet hydrogen atmosphere, the water vapor present being controllably regulated from an initial low to high level to achieve optimum expeditious results.

The specific nature of this invention, as well as other objects and advantages thereof, will become apparent to those skilled in the art from the following detailed de-



scription, taken in conjunction with the annexed sheets of drawings on which, by way of preferred example only, are illustrated the preferred embodiments of this invention.

On the accompanying drawings:

Fig. 1 is a schematic view of heating and atmosphere controlling apparatus applicable to practicing the present method of oxidation.

Fig. 2 is a perspective view of an anode button illustrative of alloy parts suited to oxidation by the prescribed method.

Fig. 3 is an enlarged fragmentary sectional view of a side wall of said anode button illustrative of its finally oxidized surfaces.

While the present invention will be described in a preferred embodiment as specially suited to preoxidizing the surfaces of chrome-iron alloy parts such as anode buttons or positioning studs for glass cathode-ray tube envelopes, it is fully understood that the principles of the invention are equally applicable to preoxidizing surfaces of other stainless steel parts for other purposes than those specifically described herein.

Referring to the drawings and particularly to Fig. 1, the oxidizing apparatus 10 is comprised of an elongated tube 11 mounted within a furnace 12 and an adjacent cooling chamber 13. The ends of the tube 11 extend beyond the respective furnace 12 and cooling chamber 13 to provide access into the tube and maintenance of controlled atmosphere therein. Furnace 12 has a heating element 14 surrounding a lengthwise portion of tube 11 in spaced relation therefrom and may be fabricated essentially of refractory material. Chamber 13 has a fluid coolant such as water supplied to inlet and outlet lines connected thereto for maintaining minimal temperatures in this area. Chamber 13 is adapted to both introduction of the parts to be oxidized and cooling of the same during latter stages of oxidation. The tube end near chamber 13 is provided with a hinged access door 15. Tube portion 16 surrounded by chamber 13 provides an area where the parts to be oxidized are flushed of their entrained air prior to oxidation, and subsequently are cooled after oxidation.

Tube end 20 is provided with several interconnecting lines 21 and 22 adapted to supply both wet and dry hydrogen gas to the oxidizing tube 11 from tanks 27 and 28 of hydrogen and nitrogen. Hydrogen tanks 27 and nitrogen tank 28 are provided with a flow regulating valves and the gas is conducted through several flow meters 25 and 26 into the tube end 20. The gas stream passing through flow meter 25 is bubbled through a water receptacle maintained at a relatively constant temperature of from about 18° to 26° C. within bath 24. The gas saturated with the water vapor at the temperature of the bath is then passed through line 22 into tube end 20. The bath temperature may be varied between the above limits, an intermediate temperature of from 20° to 21° C. being preferred.

An example of parts which may be preoxidized by the subject method is hollow frusto-conical shaped button 18 having a shape similar to that illustrated in Fig. 2. The button 18 may be fabricated of an alloy such as chrome-iron alloy having compositional designations as stainless steel Product Nos. 430 and 446.

The glass button 18 may be formed into the shape of a cup, its large open end adapted to extend exteriorly from the side wall of a glass part for engaging a connecting terminal. The button 18 may be formed of an alloy consisting of about 18.0% chromium, 0.5% nickel, 0.5% titanium, 0.40% silica, 0.35% magnesium, and other oxides of the elements of carbon, phosphorus, sulphur, aluminum in minor amounts, the remainder of the alloy or about 80% being substantially iron. The thermal expansion coefficient of this particular type of alloy is approximately  $117 \times 10^{-7}$  cm./cm./degree C. through the range of 20°-600° C.

Several other alloys which are also applicable to oxidation by the present method are listed below:

Chemical analyses of No. 446 stainless steel alloys:

	A	B
C	.12	.12
Mn	.50-.80	.50-.70
Si	.20-.50	.25-.50
P	.03	.03
S	.03	.03
Cr	27.00-29.00	28.00-30.00
Ni	.50	less than .50
N <sub>2</sub>	.10-.15	.13-.18
Cb	.60	
Fe	balance	balance
Coefficient of Thermal Expansion (20°-600° C.)	$114 \times 10^{-7}/^{\circ} \text{C.}$	$114 \times 10^{-7}/^{\circ} \text{C.}$

The above-listed alloys match the expansion coefficients of the following glass particularly well for sealing thereto. One example of such glass is one containing 58.9% SiO<sub>2</sub>; 10.3% PbO; 4.2% Al<sub>2</sub>O<sub>3</sub>; 5.8% CaO; 2.1% MgO; 1.2% BaO; 7.7% Na<sub>2</sub>O and 9.2% A<sub>2</sub>O<sub>3</sub> along with certain other minor constituents in still lesser amounts which are utilized to further control glass properties.

Each part to be sealed into glass is preoxidized in a manner about to be described for the purpose of forming mechanically strong glass-to-metal seals. Areas of the glass parts which are not employed to contact the glass in forming the seal may be freed of the oxide after the required glass-to-metal seal is effected such as to provide complete electrical contact with the parts as required.

The method consists of the following:

The chrome-iron alloy parts such as the anode buttons 18, for example, are placed within metal trays 19 which are then slid into the tube 11 in the introductory or cooled zone 16 of chamber 13. The temperature maintained within this area is below 200° F. and preferably is kept about 175° F. for the gas stream to flush away air from the surface of the metal parts.

An atmosphere of wet hydrogen is continually passed through tube 11 (from right to left as shown in Fig. 1) to sweep the air from the tube. Metal trays 19 containing the parts are retained within zone 16 for an interval of from 6 to 8 minutes as a precautionary measure to eliminate all contaminants such as the oxidizing air from contact with the parts. The atmosphere contains hydrogen gas containing a controlled amount of water vapor. About 2 to 25% of the hydrogen is saturated with water vapor at a temperature of from about 18° to 26° C. It may be preferred to pass a gas stream containing 4 to 10% of the hydrogen saturated with water vapor at a saturating temperature of from 20°-21° C. The volume of gas which is passed through tube 11 is dependent upon its size, the number of parts being simultaneously oxidized and the initial water vapor content of the gas stream. After the parts are retained within the cool zone 16 of chamber 13 for the stated period, the metal trays 19 are then pushed into the hot zone 17 of the furnace for the initial part of the oxidation cycle.

The parts are then subjected to the preferred stream of wet hydrogen containing the 4 to 10% hydrogen saturated with water vapor at 20 to 21° C. for a period of approximately 12 to 18 minutes at a temperature ranging from about 2050° to 2150° F. The prescribed small quantity of water vapor mixed with hydrogen produces a thin coating of oxide that has an exceptionally firm bond to the metal. It has been observed that when 100% of the hydrogen is saturated with water vapor during this initial stage of the oxidation cycle, the oxide produced tends to have a poor bond to the metal in glass-to-metal sealing.

The second stage of the oxidation cycle consists of further subjecting the parts to a stream of wet hydrogen containing an increased amount of water vapor for approximately 30 or 40 minutes at the stated temperature



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of from about 2050° to 2150° F. During this part of the cycle 35 to 50% of the hydrogen is saturated with water vapor at a temperature of 20 to 21° C. The saturation temperature may be varied from about 18° to 26° C. as stated, although a temperature of from 20° to 21° C. is preferred.

This quantity of water vapor present with the hydrogen supplies enough oxygen to increase the oxide weight or the thickness of the oxide film sufficiently to prevent burning and an improved joint during subsequent glass-to-metal sealing processes. It also permits conducting the oxidation at a faster rate during the secondary stage to allow economic application of the method. The weight or thickness of the oxide coating can be varied within limits dependent upon sealing requirements by changing the amount of water vapor in the hydrogen atmosphere during the primary or secondary stages of the oxidation cycle in order to secure an oxide coating of increased thickness. The greater amounts of hydrogen in the stated saturation ranges may then be utilized. In this case about 10% to 25% of the hydrogen would be saturated with water vapor during the initial oxidizing stage, while about 50% of the hydrogen would be saturated with water vapor in the secondary oxidizing stage.

The secondary oxidizing period is conducted for approximately 30 to 40 minutes and preferably about 35 minutes at the increased water vapor level.

At the completion of the second stage of oxidation the metal trays 19 are pulled from the furnace section of the tube 11 into a cooling section 16 of the apparatus. In this area the metal parts are cooled for approximately 3 to 7 minutes in a stream of wet hydrogen containing the increased amount of water vapor called for in the secondary oxidizing stage. The temperature within zone 16 at this time is below about 200° F. and preferably is about 175° F. About 35 to 50% of the hydrogen then used is saturated with water vapor at a temperature of about 20° to 21° C.

After the parts are cooled sufficiently within chamber 13 the trays 19 are removed through door 15 at the exit end of the furnace. The furnace used to practice the present invention may comprise a tubular put-through type with doors on opposite ends or may be modified in many ways to furnish advantages for commercial production. From beginning to end of the method consisting of air expulsion, heating, oxidizing, and cooling steps, a continuous flow of hydrogen gas is maintained within tube 11. The water or the oxygen content of the gaseous atmosphere during both the primary and secondary oxidizing cycles is the primary factor of the type and character of the oxide which is created on the parts. The inert nitrogen gas may be employed to regulate the rate of oxidation as required by its addition to the gas stream, serving to dilute or increase the amount of effective oxidants in the gas delivered.

Among the distinct advantages of the new method of oxidizing chrome-iron parts, a much improved oxide coating is obtainable over the metal alloy parts for improved glass-to-metal sealing. The final seals have indicated much improved characteristics over those previously made by known preoxidizing methods. Analyses of coatings created on the surface of chrome-nickel-iron alloys, for example, have shown that the coating consists of a mixture of the oxides of the metals in the original alloy.

While it is possible to vary the elevated oxidizing temperatures within the furnace section to obtain greater or lesser speeds of oxidation, temperatures being varied as much as 100° to 200° from the preferred level of about 2100° F. have been observed to cause at least some degree of degradation of the oxide to create undesirable sealing properties of the oxidized parts. An example of the oxidized film 18a over an anode button 18 is illustrated in Fig. 3.

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Various modifications may be resorted to within the spirit and scope of the appended claims.

We claim:

1. The method of preoxidizing the surface of chrome-iron alloy parts prior to sealing said parts to glass, said method comprising the steps of exposing the parts to a stream of wet hydrogen for approximately 6 to 8 minutes at a temperature below 200° F. to flush away entrained air at the surface of said parts, subjecting said parts to a stream of wet hydrogen for approximately 12 to 18 minutes at a temperature ranging from about 2050° to 2150° F. the gaseous stream comprising about 2 to 25% of the hydrogen saturated with water vapor at a temperature from about 18 to 26° C., further subjecting said parts to a stream of wet hydrogen containing an increased amount of water vapor for approximately 30 to 40 minutes at the aforesaid temperature ranging from about 2050° to 2150° F., and cooling said parts for approximately 3 to 7 minutes in a stream of wet hydrogen containing the said increased amount of water vapor at a temperature below 200° F.

2. The method in accordance with claim 1, including the step of saturating about 35 to 50% of the hydrogen with water vapor at about 18° to 26° C. to comprise the increased wet hydrogen stream during secondary subjection of the parts to a temperature ranging from about 2050° to 2150° F.

3. The method of preoxidizing the surface of chrome-iron alloy parts prior to sealing said parts into glass in vacuum-tight relationship, said method comprising the steps of exposing the parts to a stream of wet hydrogen for approximately 7 minutes at a temperature below 200° F. to flush away entrained air at the surface of said parts, subjecting said parts to a stream of wet hydrogen for approximately 15 minutes at a temperature of from about 2050° to 2150° F. the gaseous stream comprising about 2 to 25% of the hydrogen saturated with water vapor at a temperature from about 18 to 26° C., further subjecting said parts to a stream of wet hydrogen containing an appreciably increased amount of water vapor for approximately 35 minutes at the aforesaid temperature of from about 2050° to 2150° F., and cooling said parts for approximately 5 minutes in a stream of wet hydrogen containing the said increased amount of water vapor at a temperature below 200° F.

4. The method of preoxidizing the surface of chrome-iron alloy parts as a preliminary step prior to thermally sealing such parts to glass in electron-discharge devices, said method comprising the steps of exposing the parts to a controlled stream of wet hydrogen for approximately 7 minutes at a temperature below 200° F. to flush away entrained air at the surface of said parts, subjecting said parts to a gaseous stream of wet hydrogen for approximately 15 minutes at an elevated temperature of about 2100° F., the gaseous stream comprising about 4 to 10% of the hydrogen saturated with water vapor at a temperature of from about 18° to 26° C., further subjecting said parts to a gaseous stream of wet hydrogen containing an increased amount of water vapor for approximately 35 minutes at the stated elevated temperature of about 2100° F., the gaseous stream then comprising about 35 to 50% of the hydrogen saturated with water vapor at a temperature of from about 18° to 26° C., and cooling said parts for approximately 5 minutes in the stream of wet hydrogen containing the increased amount of water vapor to a temperature below 200° F., the resultant parts having stable oxidized surfaces thereover applicable to thermally sealing to glass in vacuum-tight relationship.

5. The method of preoxidizing the surface of chrome-iron alloy parts as a preliminary step prior to thermally sealing such parts to glass in electron-discharge devices, said method comprising the steps of exposing the parts to a controlled stream of wet hydrogen for approximately 6 to 8 minutes at a temperature below 200° F. to flush



away entrained air at the surface of said parts, subjecting said parts to a gaseous stream of wet hydrogen for approximately 12 to 18 minutes at an elevated temperature of about 2050 to 2150° F., the gaseous stream comprising about 2 to 25% of the hydrogen saturated with water vapor at a temperature of from about 18° to 26° C., further subjecting said parts to a gaseous stream of wet hydrogen containing an increased amount of water vapor for approximately 35-40 minutes at the stated elevated temperature of about 2050 to 2150° F., 10 the gaseous stream then comprising about 35-50% of the hydrogen saturated with water vapor at a tempera-

ture of from about 18° to 26° C., and cooling said parts for approximately 3 to 7 minutes in the stream of wet hydrogen containing the increased amount of water vapor to a temperature below 200° F., the resultant parts having stable oxidized surfaces thereover applicable to thermally sealing to glass in vacuum-tight relationship.

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