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SURFACE PREPARATION OF IRON-CHROMIUM ALLOY PARTS FOR METAL-TO-GLASS SEALS

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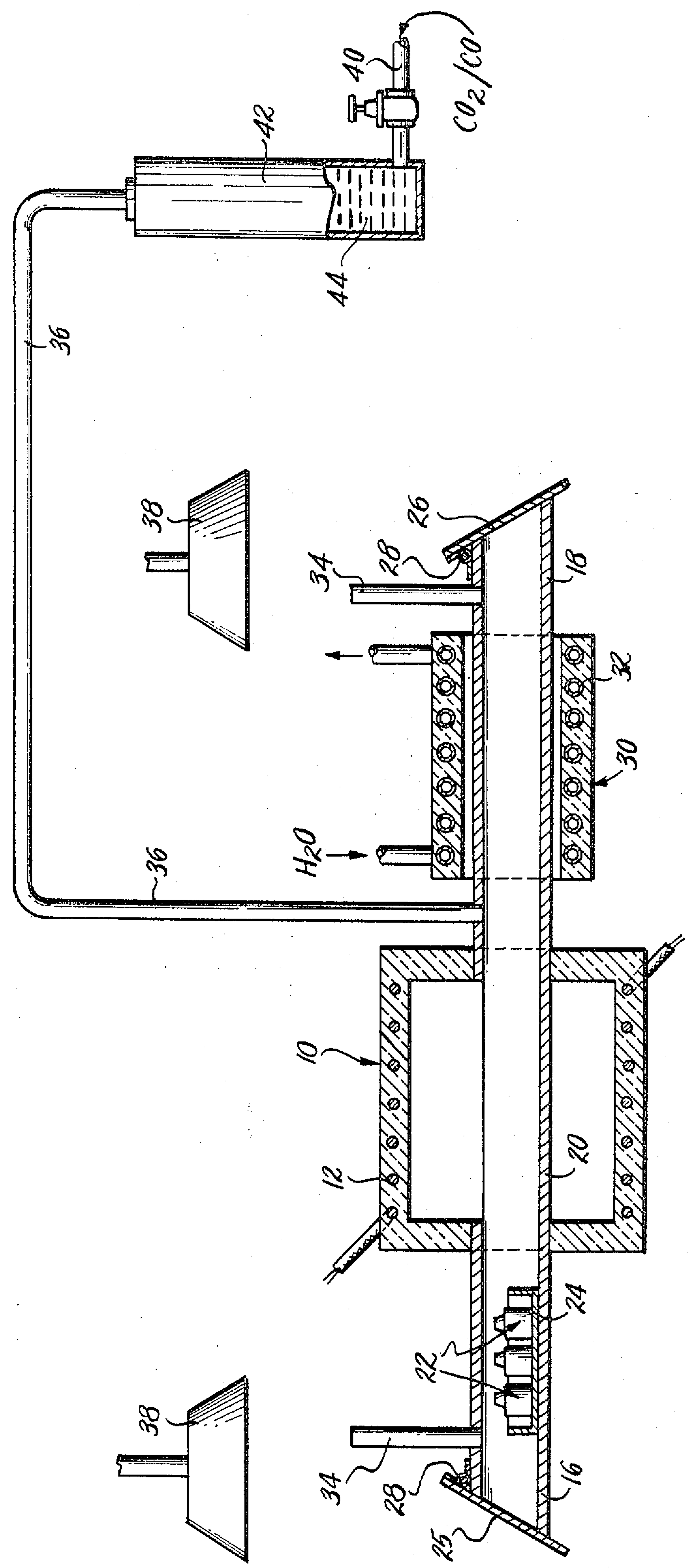

Fig. 1.

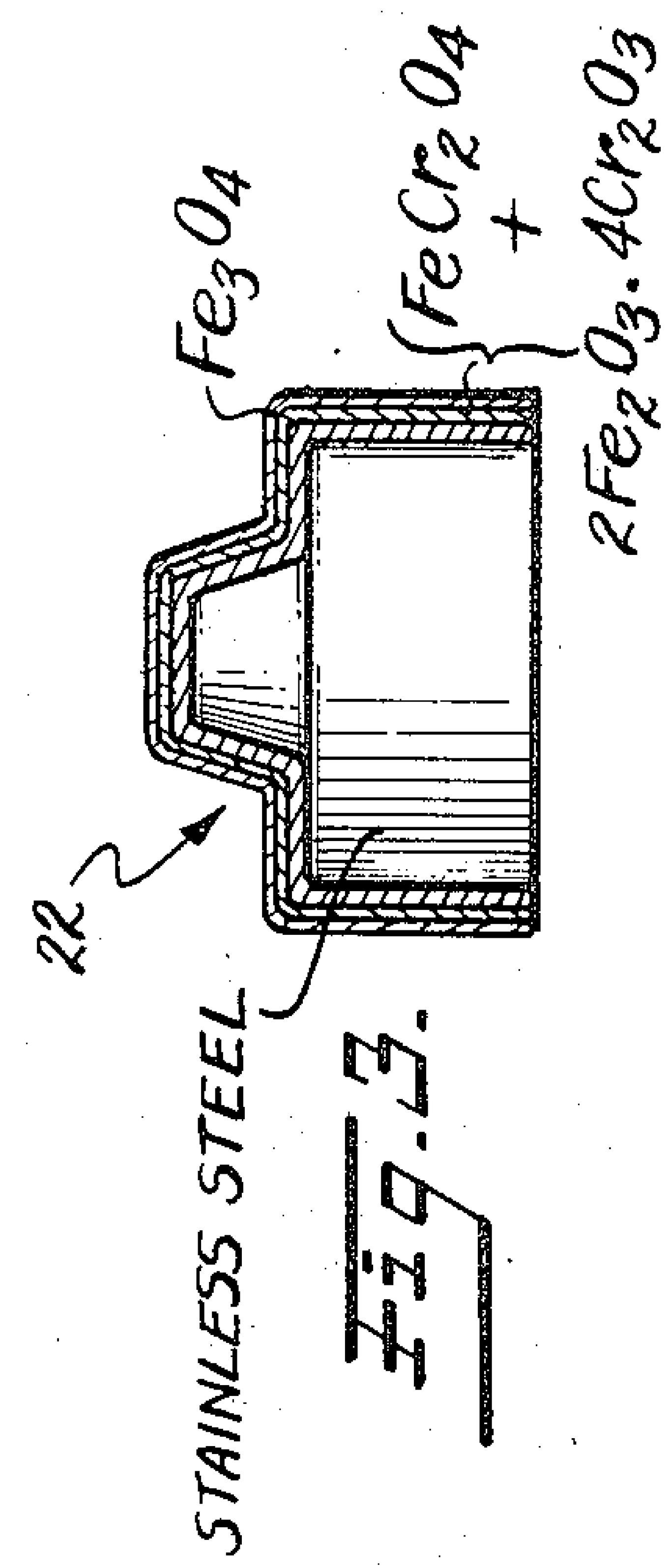

Fig. 3.

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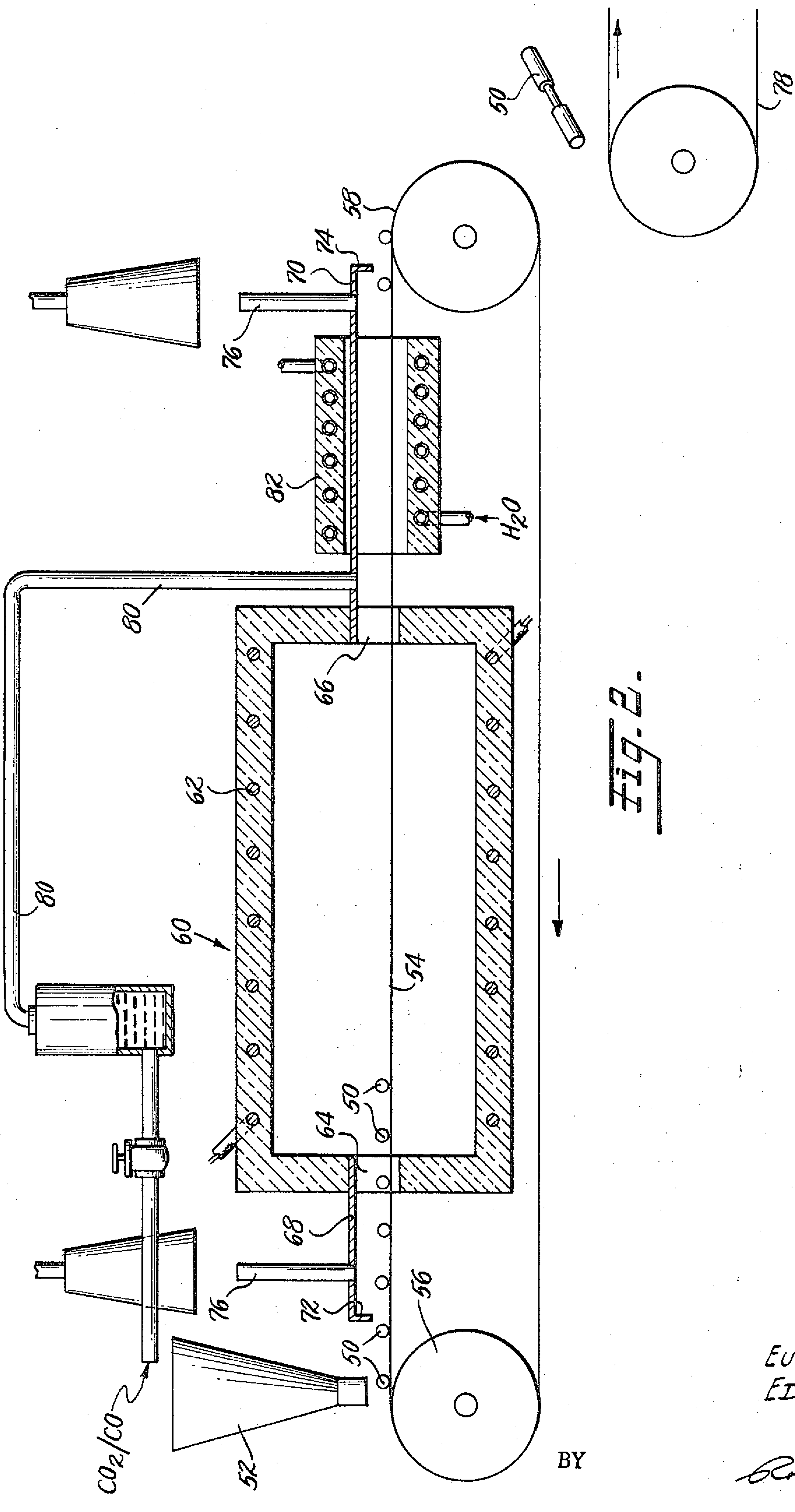

Fig. 2.

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SURFACE PREPARATION OF IRON-CHROMIUM ALLOY PARTS FOR METAL-TO-GLASS SEALS

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ABSTRACT OF THE DISCLOSURE

A new form of oxide coating on a stainless steel alloy containing a small percentage of nickel and the method of forming the oxide coating on the alloy wherein the coating is an iron chromite spinel, part of which is in a further oxidized form of a rhombohedral solid solution containing ferric oxide and chromic oxide. The method comprises treating the alloy in a high temperature oven for a prolonged period of time with a mixture of gases consisting essentially of carbon dioxide, carbon monoxide, hydrogen and water vapor in proper proportions, the mixture being obtained by cracking natural gas.

BACKGROUND OF THE INVENTION

The invention relates to an oxide coated stainless steel alloy and to the method of its production and more particularly to the oxide coating on stainless steel alloys containing a small percentage of nickel and to the method of producing the coating.

It is conventional to surface oxidize stainless steel articles that are to be sealed or bonded into associated glass mediums, for example, lead-in wires that are hermetically sealed into glass headers or closures of electron discharge devices, or the high voltage anode buttons which are sealed into the glass envelope portions of cathode ray tubes. In other instances, the oxidized alloy articles are bonded with or embedded in glass in applications where hermetic seals need not be a consideration. An example of such usage is the embedding of oxidized studs into the rim or wall portion of the face panel of a color cathode ray tube wherein the studs support the foraminous mask associated with the face panel.

The forming of a reliable and uniform high quality surface oxide is highly important in consummating tight adherence between the Cr-Fe alloy parts and the associated glass. To produce a desired oxide, specialized and expensive equipment is conventionally required wherein hazardous atmospheric materials such as liquid hydrogen or liquid ammonia are usually utilized. Even with highly specialized equipment, it is difficult to adequately control the H_2O/H_2 ratio to produce a dependable oxidation product.

Processes for oxidation of chrome-iron alloys are known and are described, for example, in the patents to Kingson 2,371,627, Brookover et al. 2,933,423 and Altman 3,185,597. However, none of these patents disclose the provision of a coating having the uniformity, tenacity of adherence to the base metal and ease of forming and other desirable characteristics, as will be pointed out hereinafter, of this invention.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the invention to reduce the aforementioned difficulties and to provide a method of producing an improved oxide coating on a stainless steel alloy article which coating, while capable of partially dissolving in glass, still leaves a film firmly adherent to the alloy metal surface, thereby enabling the creation of a vacuum tight metal-to-glass seal.

It is a further object of the invention to provide an alloy article with an oxide coating thereon which shall have the desirable properties of improved capability of fusing in with a compatible glass to form a seal therewith and yet provide improved firm adherence between the alloy base and its coating.

Another object of the invention is to provide an oxide coating on the alloy article to provide a seal to glass which does not occlude gases in the form of bubbles, nor diffuse sufficient siliceous material through the oxide to the base metal to impair the adherence of the oxide to the metal.

A further object of the invention is to provide a method which is less complicated and less expensive than conventionally utilized procedures for forming the desired oxide coating on a chrome-iron alloy.

The foregoing objects are achieved in one aspect of the invention by the provision of an improved oxide coating formed as an iron chromate spinel on a chrome-iron (stainless steel) alloy, a portion of the oxide coating being in the form of a rhombohedral solid solution of iron and chromium oxides. The coating adheres to the base metal material and remains tighly bonded thereto after being subjected to glass sealing procedures and temperatures. The discrete oxide coating is formed on the surface of the alloy by a process wherein the alloy material is treated in a high temperature oven, at a temperature/time relationship, with a proportioned mixture of gases obtained by cracking natural gas and consisting essentially of carbon monoxide, carbon dioxide, hydrogen, and water vapor.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic representation of one embodiment of the invention illustrating an apparatus for carrying out a batch oxidation process;

FIG. 2 is a representation of another embodiment utilizing a continuous oxidation process; and

FIG. 3 is an enlarged view of an oxidized stainless steel stud, the thickness of the coating being exaggerated to provide clarity of illustration.

DESCRIPTION OF THE PREFERRED EMBODIMENT

For a better understanding of the present invention, together with other and further objects, advantages, and capabilities thereof, reference is made to the following specification and appended claims in connection with the aforedescribed drawings.

The chrome-iron alloy or stainless steel utilized in these parts preferably has the composition consisting of at least 5% chromium, less than 0.15% carbon, 1.0% maximum each of manganese and silicon, no more than .5% of nickel and the balance iron except for minor traces of elements such as sulfur, phosphorous and aluminum. Obviously, other stainless steel alloys may be used in the carrying out of this invention since the essential elements of the alloy necessary to form the oxides are the iron and chromium therein.

In accordance with this invention, the operation of oxidizing chrome steel alloys may be performed by either the batch process or by a continuous operation process.

In the batch oxidation process, see FIG. 1, there is provided an oven **10** heated by any conventional means as an electric resistance element **12** embedded in walls of the oven. A horizontal chute **14**, rectangular in cross-section, traverses the oven and extends at **16** to the intake side of the oven to form a purging chamber and at **18** to the exit side of the oven to form a cooling chamber, the portion of the chute **20** within the oven having an open top for free access of heat and gaseous atmosphere to articles in the chute. The articles being oxidized as an example, may be lead-in wires for electronic tubes, to be fused into a glass header, high voltage anode buttons for electronic picture tubes, or support studs to be embedded in the flange of a face plate of a tri-color dot picture tube for supporting the perforated mask associated with the plate. The parts to be oxidized, if small, and here illustrated as support studs **22**, may be spacedly placed in a tray or boat **24** so that oxidizing gases may fully reach all parts intended to be oxidized, the boat being pushed along the chute by a rod or other means to desired locations in the chute. The ends of the chute are closed by gravity operated doors **25** and **26**, pivoted adjacent their upper ends, as at **28**. The extension **16** of the chute is large enough to accommodate one boat although it may be made long enough to accommodate a larger number of boats, such as three or more. The cut away portion **20** of the chute within the oven and the exit end **18** of the chute are also made long enough to accommodate at least one boat comfortably and, if the input end **16** is made large enough to accommodate more than one boat, the parts **20** and **18** of the chute, and the oven **10** itself, are made proportionately longer.

Surrounding the end **18** of the chute is a cooling jacket **30** with ducts **32** therein to be supplied with water or other refrigerant to cool the space within the chute portion **18**. Gas venting burners **34** are provided adjacent the free ends of the duct portions **16** and **18**.

Between the end of the cooling jacket nearest the oven and the adjacent oven wall is positioned a gas inlet pipe **36** by means of which a cracked natural gas is fed into the chute and oven. Venting hoods **38** are provided at the pivoted doors and above the venting burners **34** to carry away burned or any deleterious gases. The cracked gas is fed via a pipe **40** into a tank **42** partially filled with water **44** and thence into an expansion area above the water to provide a pressure stabilizing area for the now moist mixed gases flowing into the pipe **36**.

The natural gas is that normally fed from the gas mains to domestic and commercial users and consists of a mixture of gases containing essentially the following combustible gases: methane (CH_4), ethane (C_2H_6), carbon monoxide (CO) and propane (C_3H_8) having a B.t.u. of approximately 1040. This gas is burned in atmospheric air under controlled conditions to form the cracked gas utilized in the invention, the cracked gas having the following percentage composition:

	Percent	Preferred percent
CO_2	6–9	6.8
CO	5–10.5	7.0
H_2	4–13.0	5.5
H_2O	1–3.5	2.2
N_2	Balance	Balance

Reference is made to the patent to Kiser 2,398,012, disclosing more specifically how the gas may be cracked.

This cracked gas is much less dangerous to handle in the present oxidizing process than the dissociated ammonia and the hydrogen of previous processes. The flammability of the cracked gases in air is in the range of one tenth that of dissociated ammonia and vastly less than that of hydrogen.

At the elevated temperature of approximately 2100° F. which exists in the oven, the carbon dioxide and water vapor of the mixture dissociate into the monoxide of carbon and nascent oxygen according to the reaction (1) and hydrogen and nascent oxygen according to the reaction (2).

(1) $$2CO_2 \rightarrow 2CO + 2O^{--}$$

(2) $$2H_2O + \Delta \rightarrow 2H_2 + 2O^{--}$$

In carrying out the process of the invention, the iron and chromium in the alloy at the surface of the parts and because of the existence of the nascent oxygen are oxidized to ferrous oxide and chromium oxide according to the reactions:

(3) $$Fe + CO_2 \rightarrow FeO + CO$$

and

(4) $$2Cr + 3CO_2 \rightarrow Cr_2O_3 + 3CO)$$

Under the conditions of time and temperature as hereinafter set forth the iron and chromium oxides combine to form the iron chromite spinel $FeCr_2O_4$. With continued time, heat and further nascent oxygen, part of the spinel is further oxidized to a rhombohedral solid solution, thus forming an oxide coating extremely adherent to the base alloy and one which fuses readily into glass. The further oxidation reaction takes place according to the following:

(5) $$4FeCr_2O_4 + 2O^{--} \rightarrow 2Fe_2O_3 \cdot 4Cr_2O_3$$

Also it appears that during the continued creation of nascent oxygen the passage of some of the sesqui oxide of chromium thru the formed coating is retarded while the iron constituent of the alloy does diffuse through the coating to the surface thereof whereat it is formed into the ferrosoferric oxide Fe_3O_4.

It has been found that a good oxide which is well bonded to the metal base is composed of a high ratio of the Fe_2O_3. Cr_2O_3 rhombohedral solid solution to the cubic spinel $FeCr_2O_4$. The oxide adjacent to the metal should contain a good percentage of the rhombohedral form, preferably 35 percent or more. The balance of the surface oxide is primarily Fe_3O_4.

The glass, of course, should have a coefficient of expansion approximating that of the chrome-iron alloy. As an example, a glass of the following percentage composition has been successfully used:

SiO_2	58.9
PbO	10.3
Al_2O_3	4.2
CaO	3.8
MgO	2.1
BaO	1.2
Na_2O	7.7
As_2S_3	9.2

and traces of other oxides incidental to glass manufacture.

In the batch process the cracked gas is fed into the chute and oven at the rate per hour of 1.5 to 4 cu. ft. per square inch of cross section of the duct (and at a preferred flow of 2.5 cu. ft. per hr. per square inch of cross section of the chute). The gas is initially fed into and through the chute to thoroughly purge the unit of air. The escaping gases at the burners **34** are then ignited. The stainless steel parts are now oxidized as follows:

(1) By momentarily opening the door **25**, a loaded boat **24**, or a plurality of aligned loaded boats, are placed into the purging chamber **16** of the chute and allowed to remain there from one to three minutes, the time depending on the mass of the boat and of the parts **22** in the boats; the more mass, the longer the time. The furnace door **25** should be in the closed position after insertion of the boat and during this initial period.

(2) Then the door **25** is again momentarily opened to admit a push rod to engage the nearby boat, and thrust it (or the aligned plurality of them) into the open proper and into the center of the hot zone in the oven which is maintained at a temperature of between 2050° F. and 2150° F., preferably 2100° F.

(3) The boats are allowed to remain in the hot oven area for a period of 5 to 15 minutes, according to the mass of parts **22** and that of the boat so as to permit the parts to reach the temperature of the ambient atmosphere within the oven. This period can be determined

by the time necessary for the furnace controller, and which measures the temperature of the atmosphere within the oven, to return to the optimum predetermined interior temperature position. A period of an additional 20 to 30 minutes, preferably 25 minutes is allowed at the optimum temperature in order to develop the hitherto described oxide coating on the parts **22**.

(4) Next, the door **25** is momentarily opened to allow for the repositioning, by the use of the push rod or the like, of the boat into the cooling area **18** of the chute and to enable the placing of a second boat into the purging chamber **16** of the chute. With this process the boat in the cooling chamber is permitted to remain therein for a period of fifteen to twenty minutes depending on the mass of the boat and articles and then removed through the door **26**.

(5) The second boat, after a lapse of one to three minutes is then thrust into the oven proper and the previous continuing steps repeated.

Obviously the batch process, while effective for applying the desired coating on the stainless steel, requires considerable manipulation of doors and boats.

A preferred continuous process of handling the articles or the articles on boats is disclosed in FIG. 2. In this figure articles, such as lead-in wires **50**, are fed, seriatim, by appropriate wire feed apparatus such as is shown in the patent to Englert 2,979,228 from a hopper **52** onto a horizontal metallic wire mesh belt **54** trained over an idler roll **56** and a drive roll **58**, the latter being coupled to a motor (not shown) in a well known manner. The upper run off of the belt is surrounded intermediate its length by a heat insulated oven **60**, heated by suitable means, as electric resistance wires **62** embedded in the walls of the oven and connected to a suitable source of supply. The belt extends through openings **64** and **66** in the end walls of the oven. From these end wall openings extend open bottom boxlike shrouds **68** and **70** covering the articles on the belt but spaced from the belt a sufficient distance to allow the wires to pass beneath the end walls **72** and **74** of the shrouds. Gas venting burners **76** similar to the burners **34** in FIG. 1 are provided to burn off escaping gases, and venting hoods (not shown) may also be provided to cover the gas escape openings, as in the previous form of invention. The length of the shrouds **68** and **70**, the length of the oven and the speed of the belt **54** are such as to allow the requisite time for the articles on the belt to be subjected to purging, oxidation and cooling as in the previous form of invention. A takeoff belt **78** may be provided to move the articles to the next processing station. A cracked gas containing carbon dioxide, carbon monoxide, hydrogen and water vapor in the proportions hitherto defined, is fed at the rate defined to the space beneath the shroud **70** by means of pipe **80**. In this case, it is the cross-sectional area of the shroud which is a factor of the gas flow rate rather than the cross-sectional area of the chute. The shroud **70** and upper run of the belt adjacent thereto are surrounded by a jacket **82** cooled by a refrigerant, as water, as in the previous form of invention.

In FIG. 2 there is shown at **50** a representation of a lead-in wire in the process of being oxidized while in FIG. 3 there is shown a stud utilized for associating a face plate of a color television tube with its perforated mask, the stud being oxidized, the oxide coating being exaggerated in size for the sake of clarity of illustration.

Thus there is provided an improved oxide coating on stainless steel alloy material and an advantageous method for forming the same. The oxide coated article exhibits improved sealing with compatible glass having substantially matching thermal expansion and provides a resultant bonding joint of superior quality. The method of forming the oxide on the alloy material is accomplished with standard equipment obviating the necessity of building expensive specialized machinery. The new process utilizes less hazardous gases than those normally used by the prior art for oxidizing subject type of alloys.

While there have been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

We claim:

1. A process for oxidizing articles made of iron-chromium alloys to promote glass-to-metal bonding comprising the steps of:

forming a discrete mixture of gases resultant from the cracking of natural gas and containing as essential elements thereof carbon dioxide, carbon monoxide, hydrogen, water vapor and nitrogen, said gaseous mixture having controlled amounts of said carbon dioxide ranging from 6 percent to 9 percent of the mixture and said carbon monoxide ranging from 5 percent to 10.5 percent of the mixture;

feeding said moist mixture of controlled amounts of selected gases to an oven maintained at a temperature between substantially 2050° and 2150° F.;

positioning said articles in said oven for a period of time sufficient to form a discrete mixture of oxides thereon including the cubic spinel $FeCr_2O_4$ and the rhombohedral solid solution of $Fe_2O_3 \cdot Cr_2O_3$; and

removing said articles from said oven after a period of time during which said oxides are formed on said articles, said time varying from 20 to 30 minutes after the articles have reached the above temperature.

2. A process according to claim **1** in which the carbon dioxide comprises 6.8 percent of the mixture and said carbon monoxide comprises 7.0 percent of the mixture.

3. A process according to claim **1** in which the remaining gases comprise essentially hydrogen of from 4 percent to 13.0 percent of the mixture, water vapor of from 1.0 percent to 3.5 percent of the mixture, the balance being nitrogen.

4. A process according to claim **1** in which said natural gas before cracking, contains as elements thereof methane and ethane and has a B.t.u. of approximately 1030 per cubic foot.

5. A process according to claim **1** in which the temperature is substantially 2075° F.

6. A process according to claim **1** in which the articles are preliminarily heated in the atmosphere created in the oven, for purging of occluded gases, for a period of one to three minutes.

7. A process according to claim **1** in which the articles are cooled while subjected to the atmosphere existing in the oven for a period of 15 to 20 minutes.

8. A stainless steel article having a coating thereon, said coating being an oxide coating including a rhombohedral solid solution of oxides of iron and chromium in the form of $Fe_2O_3 \cdot Cr_2O_3$.

9. An article as defined in claim **8** wherein part of the coating is in the form of the iron chromite spinel having the formula $FeCr_2O_4$.

10. An article as defined in claim **8** wherein part of the surface coating is ferrosoferric oxide.

11. An article as defined in claim **9** having an exposed surface coating of ferrosoferric oxide.

12. An article as defined in claim **9** wherein the rhombohedral form of the coating is at least 35 percent of the rhombohedral-chromite spinel mixture.

13. An article as defined in claim **11** wherein the rhombohedral form of the coating is at least 35 percent of the rhombohedral-chromite spinel mixture.

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