

May 16, 1967

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3,320,084

VAPOR DIFFUSION PROCESS AND PROTECTION MEANS

Filed Sept. 20, 1963

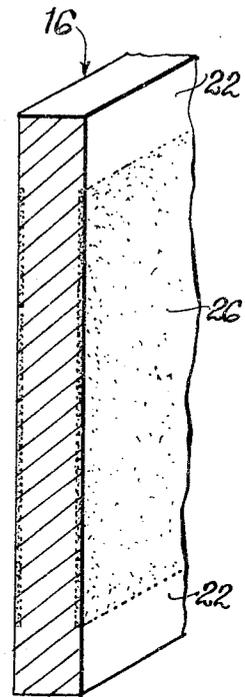
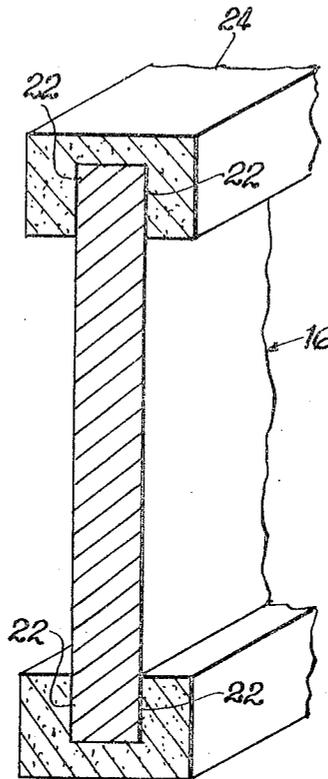
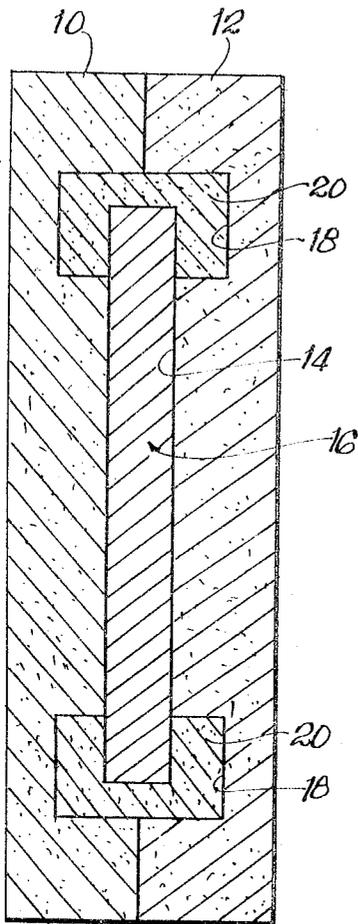


FIG. 2

FIG. 3

FIG. 1

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VAPOR DIFFUSION PROCESS AND PROTECTION MEANS

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 Filed Sept. 20, 1963, Ser. No. 310,264
 15 Claims. (Cl. 117—5.5)

This invention relates to the treatment of metals and alloys and particularly nickel base alloys or cobalt base alloys by vapor diffusion to increase the physical and mechanical properties, such for example as the high temperature corrosion resistance of the metals or alloys, and it relates more particularly to the method and means of selectively coating portions of the metal and alloy parts while protecting other portions from coating by vapor diffusion.

Metal coating by vapor diffusion to increase corrosion resistance and others of the physical and mechanical properties of alloy steels and nickel and cobalt base alloys is presently referred to as the processes of aluminizing and chromizing. Reference may be made to the following patents and applications for a more complete description of chromizing by vapor diffusion as used herein: U.S. Patent No. 2,219,005; U.S. Patent No. 2,811,466; Bunghardt et al. application Ser. No. 159,740, filed December 15, 1961; Bunghardt et al. application Ser. No. 159,742, filed December 15, 1961. Reference may be made to the following for a fuller description of the aluminizing process by vapor diffusion: Bunghardt et al. application Ser. No. 154,893, filed November 24, 1961, and Bunghardt et al. application Ser. No. 159,741, filed December 15, 1961.

In the aluminizing treatment, for example, the metal part is heated to a temperature above 1000° C. and preferably to a temperature of about 1100° C. in a powder pack of metallic aluminum and aluminum oxide or other inactive metal oxide, with or without a small amount of a halide salt, such as ammonium chloride, for about 4 to 10 hours. The powder aluminum is usually employed in a particle size of less than 5 microns and the aluminum oxide is of a particle size greater than 50 microns and more often within the range of 50–100 microns.

Under the reaction conditions described, aluminum diffuses into the surface usually to a depth of about 10 microns, depending somewhat upon the time and temperature of the aluminizing treatment. The amount of aluminum in the diffusion layer will usually average from 1 to 15 percent by weight and preferably within the range of 2 to 8 percent by weight with the concentration of aluminum decreasing from the surface inwardly towards the inner boundary of the coating.

Often times, only portions of the metal part are exposed to the corrosive gases, such as combustible gases at high temperature, whereupon it becomes more desirable to provide the protective diffusion coating to only such portions of the metal parts as are exposed to the corrosive gases while it is desirable to maintain the remainder free of the diffusion coating. Since the coating is formed by diffusion of vapors at elevated temperature, it has been difficult to block off portions of the metal parts not to be coated and such difficulties are increased in proportion to the intricacies of the shapes of the metal parts to be treated.

Thus it is an object of this invention to provide a

method and means to be used in the processes of aluminizing or chromizing by vapor diffusion whereby the coating is received by only selected portions of the metal parts desired to be protected from corrosion while other portions of the metal parts are protected from the aluminizing or chromizing vapors so that no diffusion coating will form on the protected portions whereby better and more efficient use can be made of the parts. It is a related object to provide a method and means of the type described which is applicable to metal parts of difficult configurations as well as to metal parts of normal configurations, which makes use of inexpensive and readily available materials, which can be practiced with a minimum amount of effort or utilization of a minimum amount of space, which does not in any way interfere with the normal processes of vapor diffusion to coat metal parts, which does not in any way affect or otherwise interfere with the metal part or the use ultimately to be made thereof, and which can be carried out in a simple and efficient manner.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing, in which—

FIG. 1 is a schematic cross-sectional view of the assembly mold and metal part employed in the practice of this invention;

FIG. 2 is a perspective view of the metal part embodying the protective coating applied in accordance with the practice of this invention; and

FIG. 3 is a perspective view of the metal part after treatment by vapor diffusion.

Briefly described, the concept of this invention resides in the protection of selected portions of the metal part by a coating of a ceramic material which is impervious to the chromizing or aluminizing vapors thereby to prevent exposure of the surfaces to such vapors under the elevated temperature and reaction conditions existing during the chromizing or aluminizing process and which can be applied from a fluid system to provide a protective coating which accurately conforms to the shape of the portion of the part to be protected while being located immediately adjacent the metal surface to prevent access to the chromizing or aluminizing vapors but which can be cleanly and easily removed from the surfaces of the metal part to produce products portions of which are diffusion coated while other portions are free of the diffusion coating.

It has been found sufficient to provide the protective covering in thicknesses which range from 1/16 to 1/2 inch. While a covering having a thickness of more than 1/2 inch can obviously be employed, it is economically undesirable to make use of such coverings of greater thickness by reason of the higher costs from the standpoint of the material costs and labor. A covering of sufficient thickness can be secured by the application of the coating composition from a liquid system by such conventional coating processes as dip coating, brush coating, spray coating, and the like. Where coatings of thicknesses greater than 1/16 to 1/8 inch are required or where portions to be coated are not easily accessible for dip coating, brush coating, spray coating or the like, the desired protective covering can be achieved, in accordance with an important concept of this invention, by the pro-

ess of slip casting to form a cap or covering about the portion of the metal part to be protected, using a slip casting composition and a mold cavity in communication with an absorbent surface in which moisture can be removed to set the slip casting composition about the portion of the metal part to be protected.

The following will illustrate the practice of the invention, first with compositions and methods for protection of portions of the metal part by slip casting techniques, and then by coating techniques.

Example 1

Slip casting composition:

	Parts by weight
Lithium aluminum silicate -----	3
Water -----	1

The foregoing composition will have a pH of about 9.7 and a viscosity of 10.2 seconds in a No. 5 Zahn cup.

The lithium aluminum silicate ("Lithafrax" of the Carborundum Company) is selected to have a particle size preferably of about 97% through a 325 mesh Tyler screen.

In the slip casting composition, the amount of lithium aluminum silicate may be varied preferably within the range of 2½ to 4 parts by weight of lithium aluminum silicate to 1 part by weight of water. When the ratio of lithium aluminum silicate to water exceeds 4, the composition becomes too viscous and when it is less than 2½, the slip takes too long to set and dry.

Example 2

	Parts by weight
Lithium aluminum silicate -----	60
Alumina, less than 325 mesh -----	15
Water -----	25

The foregoing again provides a solids to water ratio of 3 to 1 but the ratio of solids to water can be varied within the range of 4 to 1 as a maximum and 2½ to 1 as a minimum.

The foregoing Examples 1 and 2 constitute ceramic slips. Suitable slip casting compositions can also be formulated of powders of metals and metal oxides as illustrated by the following:

Example 3

	Parts by weight
Water -----	120
Colloidal graphite (22% solids) -----	50
Zirconia (ZrO ₂) (less than 100 mesh) -----	315
Zirconia flour (less than 325 mesh) -----	300
Nickel (less than 325 mesh) -----	265

In the above formulation of Example 3, the materials can be varied by plus or minus 20% but it is desirable to maintain the water ratio as a minimum to avoid settling of the solid materials in the slip.

Example 4

	Parts by weight
Water -----	61
Colloidal graphite (22% solids—"Aquadag") -----	16
Nickel powder (less than 325 mesh) -----	120
Chrome powder (less than 100 mesh) -----	417

Example 5

	Parts by weight
Water -----	61
Colloidal graphite (22% solids) -----	16
Nickel powder (less than 325 mesh) -----	537

With reference now to FIG. 1 of the drawing, the mold in which the slip is cast is formed of two parts 10 and 12 formed of plastic or the like materials adapted to be brought together to define a mold cavity 14 which conforms in part to the cross-section of the part 16 to be

coated by vapor diffusion and which in part 18 has walls spaced from the part 16 in the portions adapted to be protected from the diffusion vapors to provide a space 20 surrounding the portion to be protected, which space is dimensioned to have a thickness of from ¼ to ½ inch. The space 20 communicates with an opening at the top of the mold through which the slip composition is adapted to be poured and it further communicates with an absorbent surface which may constitute a part of the mold but which preferably comprises the surface on which the mold rests with the space 20 directly communicating with such absorbent surface, as by means of a continuation of the cavity. There are a number of advantages to making use of an absorbent surface on which the mold rests for the removal of liquid from the slip. For one thing, the absorption of water from the slip poured into the mold cavity is from the bottom side while the slip composition is poured from the top side so that setting of the slip will take place progressively from the bottom side up thereby to insure complete filling of the mold cavity to form the casting completely around the portions 22 of the metal part to be protected. For another, the maintenance of proper absorbency in the mold is eliminated as a problem since the absorbent surface on which the mold rests can be easily and quickly interchanged to maintain proper absorbency. Still further, with the absorbent portion being provided separate and apart from the mold, the mold parts can be fabricated of plastic materials or of other less expensive and easily shaped materials which have greater life, greater strength and greater dimensional stability while enhancing the handling of the mold parts and the separation thereof one from the other and from the casting. For such purposes, it is often also desirable to make use of a parting compound between the mold parts such as a silicon fluid or a talc referred to in the trade as "Lubikold."

In practice, the metal part 16 is assembled in the cavity 14 of the mold. The mold is positioned on the absorbent slab. A slip composition selected of Examples 1 to 5 is poured into the mold cavity to fill the mold space 20 about the mold part 22.

As moisture is absorbed from the slip composition into the walls of the mold (when use is made of a mold having absorbent walls), or into the slab, the slip sets as a casting or cap 24 about the metal part 18.

The mold parts 10 and 12 are separated to free the metal part 16 with the slip casting 24 present as a protective covering on the surfaces 22 to be protected. The separated composite is then dried, preferably at elevated temperature in the range of 200-300° F. for from 2 to 16 hours.

The formed part can then be packed with the conventional materials for vapor diffusion and then loaded into the furnace for treatment in the standard chromizing or aluminizing processes. The casting 24 formed on the portions 22 of the metal part 16 is fired at the temperature conditions existing in the furnace while, at the same time, the unprotected surfaces of the metal part are provided with the desired diffusion coating. After the chromizing or aluminizing process has been completed, the parts are removed from the furnace and the casting 24 is broken away from the metal parts to expose an underlying surface 22 which is entirely free of the vapor diffusion coating formed by aluminizing or by chromizing while the uncovered portions have the desired diffusion coating 26.

Since the protective covering is effective to block penetration of the diffusion vapors, even when present in thicknesses as little as ¼-inch, it will be apparent that one can achieve a rather sharp cut-off between the portion to receive the diffusion coating and the portions to remain as originally fabricated without the diffusion coating.

The foregoing slip cast compositions have been formulated of ceramic or metallic materials to provide a composite protective casting having a coefficient of expansion

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and contraction which is substantially similar to that of the metal of which the part is formed with the result that pressures are eliminated during the heating and the cooling cycles which might otherwise cause cracking. Thus the materials can be used without the requirement for high strength in the casting that is poured which otherwise might result in deformation of the metal part under the conditions existing in the vapor diffusion coating process.

Instead of forming the protective covering by slip casting, the metal part can be dipped one or more times into one of the compositions of Examples 1 to 5 to wet the surface with the coating composition. When one or more layers are to be incorporated into a composite coating, it is desirable to provide for intermediate drying between the applications of the coating composition until a covering of the desired thickness of $\frac{1}{16}$ -inch or more is achieved. For such purpose, the slip casting compositions of Examples 1 to 5 may be used as formulated but it is preferred to increase the fluidity by the introduction of additional amounts of water to provide for the desired consistency for dip coating, brush coating, spray coating and the like.

Aside from the described methods of application, the other procedural steps of drying, firing and removal of the covering are substantially the same as described for slip casting.

It will be apparent from the foregoing that I have provided a simple and efficient means for effecting vapor diffusion coating of selected portions of metal parts required to be protected against corrosion while other portions of the metal parts free from exposure to the corrosive gases are protected so as to maintain the original state notwithstanding the exposure of the entire part to the processes of vapor diffusion. Thus selected portions of the metal part may be provided with a diffusion coating while other portions are maintained free of the diffusion coating to retain the original characteristics at the metal surface whereby better and fuller utilization might be made of the part for the purposes intended.

It will be understood that changes may be made in the details of construction, arrangement and operation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coating on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions of the metal part with a layer of a composition selected from the group consisting of lithium aluminum silicate, lithium aluminum silicate in admixture with an oxide of a metal selected from the group consisting of aluminum and zirconium, and graphite in admixture with a material selected from the group consisting of nickel, chromium and an oxide of a metal selected from the group consisting of zirconium and aluminum in finely divided form, said layer having a thickness of at least $\frac{1}{16}$ -inch.

2. The process as claimed in claim 1 in which the finely divided materials are applied as a slip of the solid materials in aqueous suspension which has been slip cast about the other portions of the metal part to form a cap thereon.

3. The process as claimed in claim 1 in which the materials in the covering are applied from an aqueous composition by coating the composition directly onto the other portions of the metal part.

4. The process as claimed in claim 1 in which the covering layer is fired simultaneously with and at the elevated temperature for diffusion coating.

5. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coat-

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ing on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions with a layer of lithium aluminum silicate to a thickness of $\frac{1}{16}$ to $\frac{1}{2}$ inch.

6. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coating on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions with a coating of lithium aluminum silicate and alumina in admixture with the coating having a thickness of at least $\frac{1}{16}$ -inch.

7. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coating on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions with a layer of zircon, nickel and colloidal graphite in admixture in finely divided form and wherein the coating has a thickness from $\frac{1}{16}$ to $\frac{1}{2}$ inch.

8. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coating on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions with a layer of nickel, chromium and colloidal graphite in admixture in finely divided form, and wherein the coating has a thickness from $\frac{1}{16}$ to $\frac{1}{2}$ inch.

9. In the process of chromizing and aluminizing metal parts by vapor diffusion to provide a vapor diffusion coating on the surface of the metal parts, the improvement whereby, when the metal part is exposed entirely to the vapor diffusion treatment for chromizing or aluminizing, only selected portions of the part are coated while other portions are protected from the vapors to prevent formation of the diffusion coating, consisting of covering said other portions with a coating formulated of nickel and colloidal graphite in admixture in finely divided form and wherein the coating has a thickness of from $\frac{1}{16}$ to $\frac{1}{2}$ inch.

10. A metal part having portions thereof covered to prevent formation of a coating by vapor diffusion, said covering consisting of a layer of material selected from the group consisting of a composition selected from the group consisting of lithium aluminum silicate, lithium aluminum silicate in admixture with an oxide of a metal selected from the group consisting of aluminum and zirconium and graphite in admixture with a material selected from the group consisting of nickel, chromium and an oxide of a metal selected from the group consisting of zirconium and aluminum in finely divided form, said layer having a thickness of at least $\frac{1}{16}$ -inch.

11. A metal part as claimed in claim 10 in which the covering of portions of the metal part comprises lithium aluminum silicate.

12. A metal part as claimed in claim 10 in which the covering of portions of the metal part comprises lithium aluminum silicate and alumina in admixture.

13. A metal part as claimed in claim 10 in which the

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covering of portions of the metal part comprises nickel, zircon, and colloidal graphite in admixture.

14. A metal part as claimed in claim 10 in which the covering of portions of the metal part comprises nickel, chromium and colloidal graphite in admixture.

15. A metal part as claimed in claim 10 in which the covering of portions of the metal part comprises colloidal graphite and nickel in admixture.

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