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METHOD OF APPLYING A CHROMIUM COATING TO HIGH  
TEMPERATURE RESISTANT MATERIALS  
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Fig. 1.

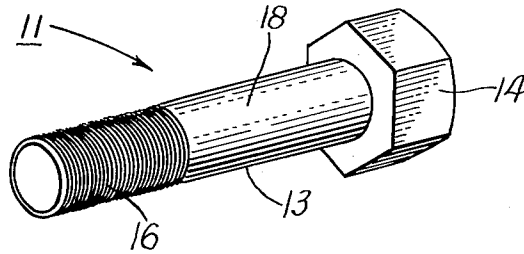
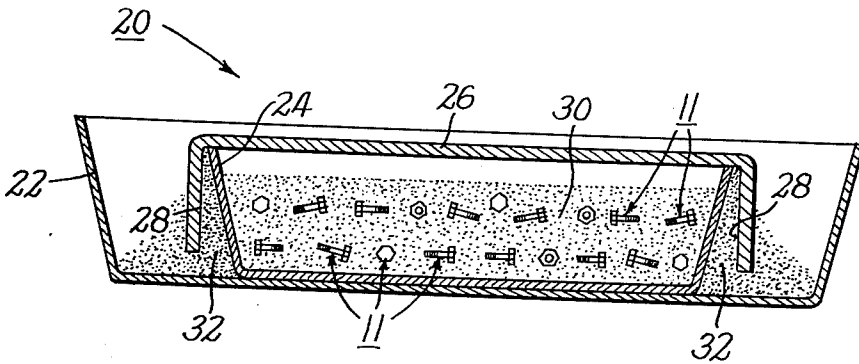


Fig. 2.



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**METHOD OF APPLYING A CHROMIUM COATING TO HIGH TEMPERATURE RESISTANT MATERIALS**

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Continuation of application Ser. No. 505,468, May 2, 1955. This application Jan. 7, 1960, Ser. No. 2,796 7 Claims. (Cl. 117-107)

This invention generally relates to processes for applying a layer or casing of a metal upon a dissimilar base. More particularly, it relates to chromizing heat resistant materials or metals, such as molybdenum or tungsten, with or without alloying constituents, by diffusion techniques at high temperatures. This application is a continuation of our copending application Serial No. 505,468 filed May 2, 1955, and now abandoned.

While, for example, it has been recognized that molybdenum exhibits excellent strength and anti-creep properties at temperatures of the order of 1500°-2400° F., heretofore difficulty has been encountered in using molybdenum at such temperatures. This is due primarily to the formation of a volatile oxide of molybdenum and consequently its low resistance to oxidation. Otherwise stated, molybdenum parts have a tendency to become destroyed at high temperature conditions because of volatilization of an oxide of molybdenum from the surface thereof. This undesirable characteristic of molybdenum has prevented widespread use in oxidizing conditions of articles made of molybdenum or made of high molybdenum alloys as well as to a somewhat lesser extent in the case of the low iron content, high molybdenum, high nickel or high cobalt content alloys. Similar difficulties in service have occurred with certain materials termed cermets, i.e. hard ceramic-metal materials such as titanium carbides as well as the borides of these elements.

Attempts have been made to coat the materials referred to above with an oxidation resistant metal such as chromium by using various techniques of electroplating. These attempts have met with indifferent success as such materials are frequently very difficult to chromium plate at all; moreover when an electro plate of chromium has been placed on such bases, not only is the coating more or less unevenly distributed but the coating is rather porous and has a tendency to blister at high temperatures. Additionally, electro plated chromium, in common with dip coatings, significantly increases the dimensions of the finished article to a degree generally considered undesirable in parts of close tolerances.

As has already been noted in our copending application Serial No. 505,565 (now Patent #2,837,442), there is also an aspect of appearance in the coating of molybdenum parts. Thus, according to the foregoing patent application, a more or less shiny surface is achieved on molybdenum parts treated with a diffusion coating of chromium if there is specifically added to the chromizing pack or otherwise incorporated in the diffusion coating a small proportion of iron, which small iron proportion provides a shiny coating of enhanced appearance. The presence of this small proportion of iron in the finished coating on the molybdenum article, however, may, under certain circumstances of use at particularly high temperatures, etc., provide an entrance or inroad for corrosion or oxidation. Accordingly, in situations where the appearance of the article is of less importance than the ultimate oxidation resistance thereof, as in accordance with this invention, enhanced results have been found to be achieved by taking steps to avoid any presence of iron or ferrous materials in the pack or step of diffusion

coating of chromium into molybdenum and other non-ferrous metals in accordance herewith, although the resulting coating does have a duller and less shiny appearance than when some diffusion coated iron is included therein.

It is, accordingly, an object of the present invention to overcome the above-mentioned difficulties and disadvantages of known methods of applying a chromium-rich layer on heat resistant base materials, which chromium layer is applied substantially in the absence of ferrous infiltration. It is a further object of the invention to provide chromized articles of heat resistant base materials which are not only resistant to corrosion and oxidation over a wide range of temperatures but wherein the chromium layer does no change the dimensions of the piece materially. Further objects and advantages of the invention will be in part pointed out and in part apparent as this specification proceeds.

Before describing our invention further it is to be noted that the recitation of the details of specific embodiments of the invention is generally intended to be illustrative of the invention and not limiting thereof, the limits of the invention being indicated with more formal particularity in the appended claims.

In one of its broader aspects the invention may be said to lie in chromizing articles of the said base materials while said articles are maintained at an elevated temperature and are maintained in the presence of a finely divided mixture of inert filler, metallic chromium or a material rich in metallic chromium and a minor quantity of a halide compound such as ammonium iodide. It is a feature of the invention that, while the chromizing treatment is maintained, formation of undesired chromium oxides and diffusion of less corrosion-resistant ferrous components are avoided or at least minimized. In one embodiment of the invention, there is employed as the chromizing pack a mixture of baked kaolin or other substantially moisture free mineral filler material such as anhydrous alumina, powdered chromium, whether pure or of commercial grade provided it is substantially pure and free of iron (i.e., utilizing as the source of chromium substantially pure metallic chromium or readily reducible chromium salts or alloys other than such iron-containing materials as ferrochromium), and a fractional percentage of ammonium iodide. During the heating there is thus avoided on the one hand too low a concentration of chromium in the pack and on the other hand too high a concentration of water vapor which would tend to oxidize the chromium in the chromizing pack, and, in any case, the presence in the pack of a source of iron which might, inadvertently, also be diffused along with the chromium into the surface of the article being treated to provide a point of entrance of undesired corrosion at the elevated temperatures of use.

Perhaps the features of the invention may best be understood and appreciated by reference to the accompanying drawings wherein:

FIG. 1 is a view of a high temperature bolt of molybdenum, which typifies an article of close tolerances to be chromized according to the invention; and

FIG. 2 is an internal view of a retort used in chromizing.

Referring more particularly to the drawings, in FIG. 1 is shown a bolt generally designated 11 having a shank 13, a hexagonal head 14 and a threaded portion 16. Upon treatment a surface coating 18 of a chromium-molybdenum alloy is formed, the proportion of chromium in the surface alloy decreasing with increasing depth into the body of the bolt 11. In this regard it is to be observed that the thickness of the surface coating 18 is largely dependent upon the temperature and time of the treatment, higher temperature and lengthy periods of

treatment in general increasing the surface coating to a feasible maximum of about 0.006 inch.

In FIG. 2 there is shown a chromizing retort 20 comprised of an outer lower tray 22, an inner tray 24 and a lid or cover 26. Within inner tray 24 is placed a plurality of articles, e.g. bolts 11, to be chromized; these are surrounded with the powdered chromizing pack of mixture. The apertures or openings 28 between lid 26 and inner tray 24 contain a liquid or liquifiable seal which minimizes the efflux of evolved gases as the operating temperatures are attained and also prevents leakage of unwanted air into the inner tray 24 as the retort 20 is cooled, and, as will be understood from the foregoing, it is preferred that retort 20 be formed of a non-ferrous or non-iron-containing material to avoid the possibility of inadvertent diffusion coating into the surface of the articles 11 being coated any significant or substantial portion of iron along with the desired chromium diffusion.

Turning now to a particular example, molybdenum bolts 11 are placed in inner tray 24 and then surrounded with the chromizing pack 30, which is comprised of about 35% by weight of baked kaolin, about 65% of chromium and less than 0.5% of ammonium iodide. The entire pack is comminuted to pass 100 mesh (Tyler standard screen) and thoroughly mixed. Care is taken that the surfaces of the bolts 11 are clean; if not originally clean, they are subjected to a preliminary cleaning treatment using known methods. After surrounding bolts 11 with the chromizing pack 30, inner tray 24 is placed inside of outer tray 22 and cover or lid 26 placed over the inner tray. Next, fusible silicate 32 is placed in the apertures or exit passageway 28 between inner tray 24 and cover or lid 26 and also to some extent in the space between cover lid 26 and outer tray 22.

Thereupon the entire retort 20 is placed in a furnace of suitable design such as a well insulated gas-fired furnace. Typically about 4-14 hours elapse before retort 20 reaches the desired chromizing temperatures of about 1900° F. The retort is maintained at the chromizing temperature for about 6 to 18 hours, depending upon the depth of penetration desired in the final chromium-rich casing on the bolts. Next the retort 20 is removed from the furnace and allowed to cool.

After cooling, the feed silicate seal 32 is broken and lid or cover 26 removed from the inner tray. Bolts 11 are then removed from the residual chromizing pack. It should be noted that, although parts of the pack 30 become somewhat more granular or lumpy, this does not indicate deterioration of the pack as we have found that a given virgin pack may be used for several treatments, the residual pack being mixed with sufficient additive pack rich in chromium and ammonium iodide to raise the content of active ingredients of the admixed pack to the optimum value. Moreover, even though some caking or sintering of the pack occurs during the high temperature treatment, the chromized parts are easily removable from the pack without stickiness or adhesion of the pack to the final chromized product.

It will be observed that in the example described the moisture content of the chromizing pack is minimized by using baked kaolin in as much as the high concentration of chromium in the pack is quite sensitive to oxidation by water vapor. Using a pack containing about 65% chromium and about 35% filler, it was found that about 3% moisture (based on the total pack) represented the maximum amount of water which could be tolerated without substantial oxidation during treatment. In one specific example, when unbaked kaolin having some 14% moisture (measured by ignition loss test) was employed, the water vapor content of the retort atmosphere was so high that the metallic chromium in the pack turned green due to excessive oxidation, and deposition of the desired satiny or dull or iron-free chromium layer on the molybdenum work piece was inhibited to an extent making further treatment with such packs not feasible.

With packs containing lesser proportions of chromium, e.g. about 50% metallic chromium and 50% inert fillers such as clays, somewhat more moisture may be present in the pack, the precise maximum being determined for each specific mix by one or more test runs. It is to be noted that some 5% total moisture will generally be found to be the upper limit for the packs less rich in metallic chromium. Increasing dilution of the metallic chromium content of the pack yields poor or negligible coating of the base but a lessened tendency for adhesion of pack particles to the base material. Consequently we insure that, in any event, the moisture content is kept at a minimum value since higher moistures serve no useful purpose and are in fact, quite deleterious. As will be understood, of course, the utilization of more or less anhydrous alumina instead of baked kaolin or clay mentioned, forms a satisfactory, and, indeed, preferred filler for controlling and maintaining the desired moisture-free atmosphere during the coating step in accordance herewith.

Again, one may on occasion mix in the pack small quantities of additives which tend to absorb or combine with water vapor in the retort atmosphere and thus decrease the oxidation tendency thereof. Among such additives are titanium, zirconium, the halides or hydrides therein and like materials which are reactive with H<sub>2</sub>O at high temperatures.

While in the above examples, we have referred to the use of kaolin in the pack, other inert fillers, as noted, such as porcelain, various clays, alumina, titanium oxide and chromite (Cr<sub>2</sub>O<sub>3</sub>) may also be utilized.

Another feature of the invention lies in the elimination from the chromizing pack of small amounts of an elemental halogen. We have found that a small quantity of ammonium iodide as indicated above is sufficient to produce a good casing of chromium and that prior addition of elemental halogens to the pack is not essential. halogens to the pack is not essential. Moreover, in addition to ammonium iodide, one may use other halides such as ammonium bromide and ammonium fluoride and bifluoride, bearing in mind that care must be exercised in using fluorides due to possible poisonous effects on personnel. While chlorides offer certain advantages due to low cost, we prefer to employ the other halides mentioned.

We also find that a given pack may be re-used for several chromizing treatments provided that the chromium and halide content is replenished. For example, we have found good results may be attained if about one part of virgin pack enriched in chromium and halide is thoroughly mixed with about four parts of used pack, when the total surface area of the work to be chromized is high relative to the volume of the pack. However, other ratios of virgin pack may also be used depending upon the requirements of a particular treatment.

Although the invention is particularly useful in chromizing molybdenum, other heat resistant bases may also be chromized in accordance with our treatment. Among such additional bases are certain cermets, that is intermetallic compounds, particularly sintered carbides and borides such as titanium carbide, tungsten carbide, tantalum carbide, zirconium boride, chromium boride, titanium boride and combinations thereof. In the case of cemented titanium carbide, the technique of chromizing is similar to the chromizing of molybdenum as described above, the resulting treated product having a smooth, uniform, dull gloss coating which is believed to be a chromium alloy with the base. It is to be noted that a further advantage of chromizing cemented titanium carbides according to the invention is that one may thereby avoid the use of nickel as a binder and use less expensive and less scarce iron instead.

Also to be found among the base materials which may be chromized according to the invention are certain high nickel or high cobalt content alloys, which are generally regarded as non-ferrous (hereinafter referred to as sub-

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stantially non-ferrous) because the iron content of these alloys is quite small, and enhanced corrosion resistance is achieved by the specific elimination of various components which might be diffusion coated from constituents of the pack into the articles being coated. A specific example of such an alloy is known under the name of Hastelloy B, commercially available from the Haynes-Stellite division of Union Carbide and Carbon Corporation. The composition of Hastelloy B is believed to be 65% Ni—28% Mo—5% Fe and 0.4% V. Another specific example is the alloy known as S-816, available from Alleghany-Ludlum Steel Company; the composition of this alloy is believed to be 43.7% cobalt—20% nickel—20% chromium—0.4% carbon—4% molybdenum—4% tungsten—2.8% iron—3.75% columbium.

Chromizing of these cements and high cobalt or high nickel alloys enhances their corrosion or oxidation resistance at high temperatures while still preserving their excellent strength characteristics and particularly if the chromizing step is conducted under the circumstances, as disclosed above, whereby inadvertent diffusion of iron into the coating layer is avoided.

Having now particularly described various embodiments of our invention, what we claim is:

1. The method of applying an essentially iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is maintained in the presence of a powdered chromizing pack of less than 5% initial moisture content, said pack being essentially free of iron and comprised of a fractional percentage of a source of a gaseous halide, chromium and an inert filler, whereby a chromium coating having increased oxidation resistance is provided.

2. The method of applying an essentially iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is in contact with a powdered chromizing pack which is essentially free of iron, said pack being comprised of a very small quantity of ammonium iodide, chromium and kaolin, the initial moisture content of said pack being less than 3%, whereby a chromium coating having increased oxidation resistance is provided.

3. The method of applying an essentially iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is embedded in a powdered chromizing pack, said pack being essentially free of iron and comprised of a fractional percentage of an ammonium halide, about 65% chromium and about 35% baked kaolin, the initial moisture content of said pack being less than 3%, whereby

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a chromium coating having increased oxidation resistance is provided.

4. The method of applying an essentially iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is embedded in a powdered chromizing pack, said pack being essentially free of iron and comprised of a fractional percentage of an ammonium halide, about 50% chromium and about 50% baked kaolin, the initial moisture content of said pack being less than 5%, whereby a chromium coating having increased oxidation resistance is provided.

5. The method of applying an essentially iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is embedded in a powdered chromizing pack which is essentially free of iron, said pack being comprised of a fractional percentage of an ammonium halide, about 50-75% chromium and about 25-50% baked kaolin, the initial moisture content of said pack being less than 5%, whereby a chromium coating having increased oxidation resistance is provided.

6. The method of applying an iron-free chromium coating to a high temperature resistant material selected from the class consisting of molybdenum, non-ferrous alloys of molybdenum, metallic borides, metallic carbides, high nickel content substantially non-ferrous alloys and high cobalt content substantially non-ferrous alloys which comprises subjecting said material in a non-ferrous retort to an elevated temperature for a protracted period in a substantially oxygen-free atmosphere while said material is in the presence of a powdered chromizing pack, said pack being free of iron and comprised of a fractional percentage of an ammonium halide, chromium, an inert filler and a minor quantity of water absorbent material, whereby a chromium coating having increased oxidation resistance is provided.

7. The method according to claim 6 wherein said latter named material is selected from the class consisting of titanium, zirconium, an oxidizable zirconium compound.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

1,497,417	Weber	June 10, 1924
1,711,603	Lay	May 7, 1929
1,853,369	Marshall	Apr. 12, 1932
2,219,005	Davies et al.	Oct. 22, 1940
2,536,774	Samuel	Jan. 2, 1951
2,622,043	Roush	Dec. 16, 1952
2,811,466	Samuel	Oct. 29, 1957
2,825,658	Samuel	Mar. 4, 1958
2,874,070	Galmiche	Feb. 17, 1959
2,875,090	Galmiche	Feb. 24, 1959

##### FOREIGN PATENTS

160,812	Australia	Jan. 28, 1955
744,355	Great Britain	Feb. 8, 1956

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,065,108

November 20, 1962

Richard P. Seelig et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 15, for "no" read -- not --; column 3, line 44, for "feed" read -- fused --.

Signed and sealed this 30th day of July 1963.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

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