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FORMATION OF DIFFUSION COATINGS ON NICKEL CONTAINING
DISPERSED THORIA
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3,764,371

Fig. 1.

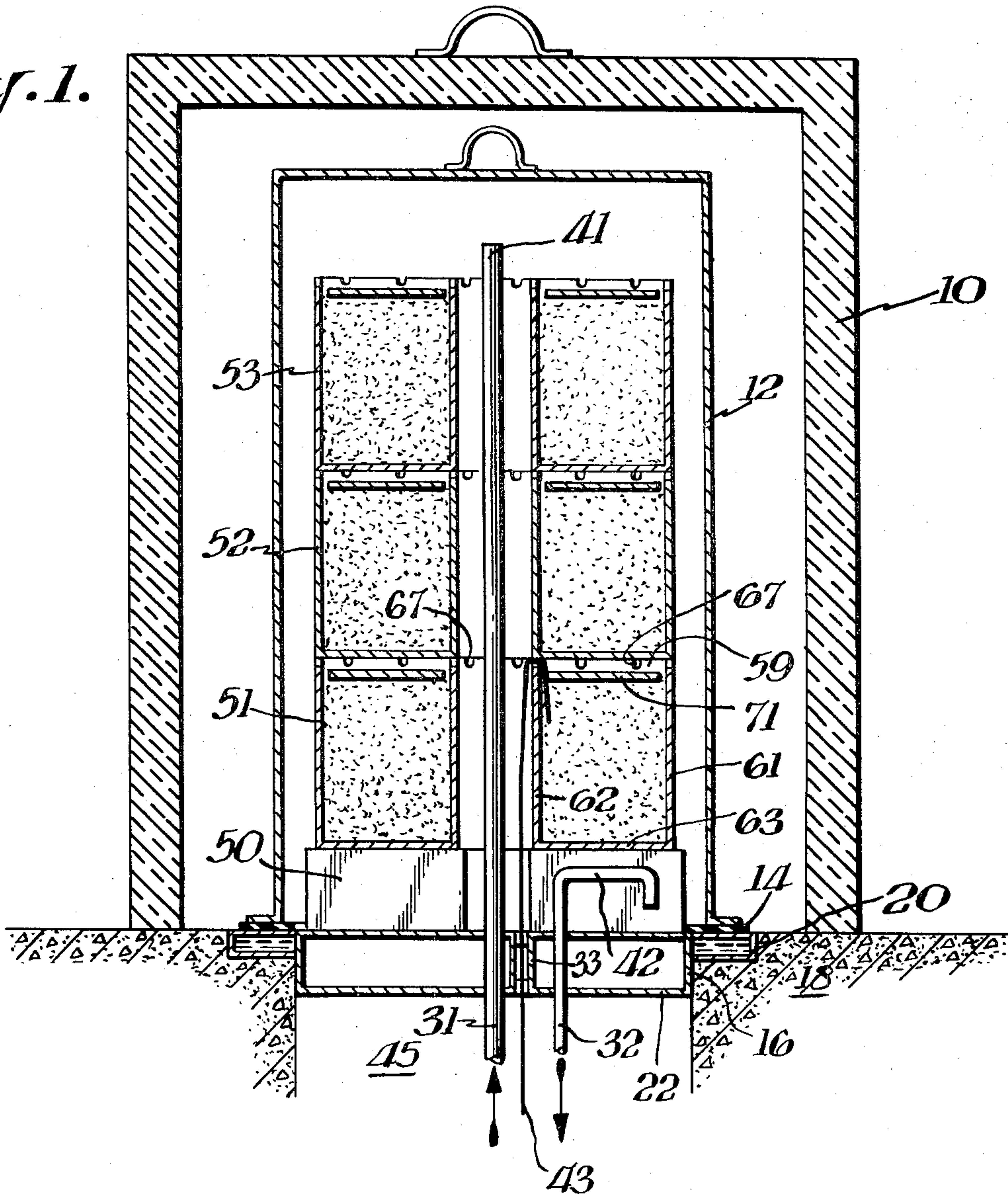
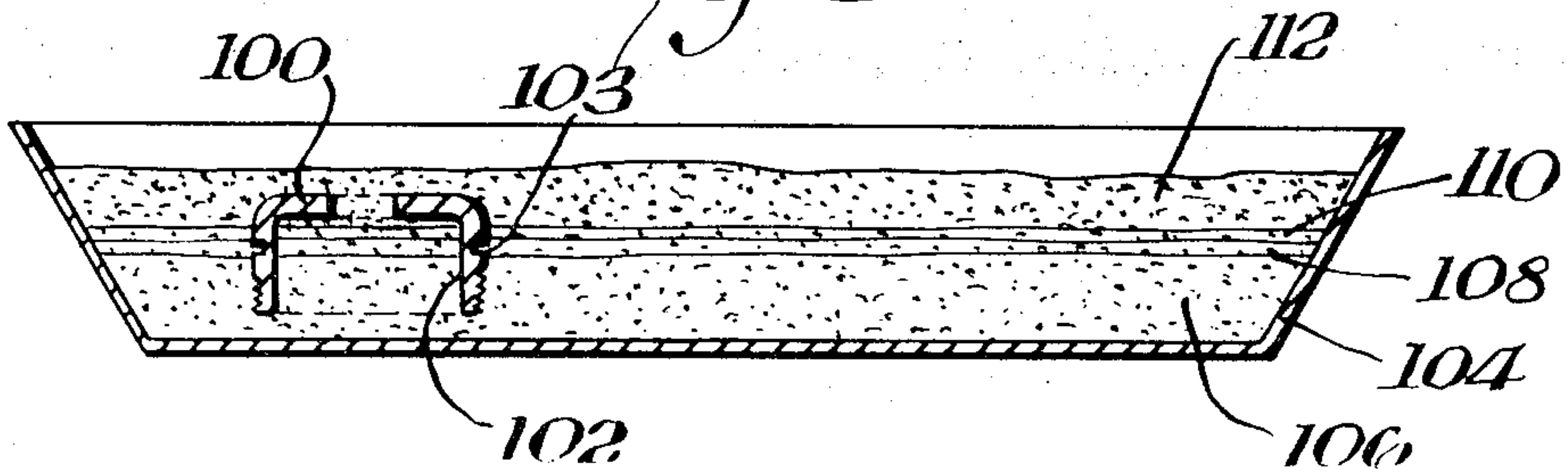


Fig. 2.



1

3,764,371

FORMATION OF DIFFUSION COATINGS ON NICKEL CONTAINING DISPERSED THORIA

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U.S. Cl. 117—71 M

11 Claims

ABSTRACT OF THE DISCLOSURE

Rich chromium diffusion coating on TD nickel or TD Nichrome is obtained in one step by embedding work in chromium diffusion coating pack containing nickel with or without some cobalt, and held in unsealed retort cup at least 15 inches high. Magnesium halide is helpful to have in the pack and pack can also contain metallic iron to reduce coating temperature. Masking is arranged by covering the sites to be masked with a layer of a mixture of nickel powder and inert filler. For better high temperature oxidation resistance the chromium-rich coating is covered by an aluminum diffusion coating from a simple aluminum diffusion pack or one that has the aluminum mixed with chromium. Low temperature aluminum diffusion is more uniform when pack energizer is aluminum chloride or other material that does not generate nitrogen. A manganese-containing aluminizing pack gives better protection than a simple aluminizing pack, particularly against marine corrosion, and when there is a conversion coating applied over the aluminizing. Conversion coating mixture wets aluminized ferrous surface better when the surface has been treated with alkali to blacken it, and the black is then removed with the help of nitric acid. Aluminized superalloy can be heated in air to whiten it, then cleaned to give product having more adherent case. Also adding some lanthanum or yttrium to superalloy like WI 52 gives better high temperature resistance.

This application is in part a continuation of application Ser. No. 837,811 filed June 30, 1969 and now abandoned.

The present invention relates to the diffusion coating of TD nickel and other high temperature materials.

Thoria-dispersed nickel, more commonly called TD nickel, and thoria-dispersed Nichrome, similarly called TD Nichrome, are unusual materials, particularly at high temperatures. They have greater structural strength at temperatures of about 2300° F. than nickel- and cobalt-based superalloy. However it has been difficult to adequately protect the TD nickel and TD Nichrome against excessive oxidation at such high temperatures.

It has been known that good oxidation protection is provided by first diffusion coating the TD nickel with 40 to 60 milligrams chromium per square centimeter of surface, followed by a diffusion coating of 1.5 to 4 milligrams aluminum per square centimeter. Unfortunately the heavy chromium coatings have been difficult to obtain in a readily reproducible satisfactory form without using two separate chromium diffusion operations.

Among the objects of the present invention is the provision of improved coating techniques for TD nickel and related materials.

The foregoing as well as other objects of the present invention will be more fully understood from the follow-

2

ing description of several of its exemplifications, reference being made to the accompanying drawings in which:

FIG. 1 is a vertical sectional view of a diffusion coating set-up pursuant to the present invention; and

FIG. 2 is a similar view of a related masked diffusion coating operation.

According to the present invention a rich chromium layer of high quality is diffused into TD nickel or TD Nichrome articles in one step from a pack held in an unsealed retort cup at least 15 inches high, and the pack contains 5 to 40% chromium as well as nickel in a proportion from about $\frac{1}{3}$ to about $\frac{1}{20}$ of the chromium. The pack can also contain cobalt in an amount from about $\frac{1}{20}$ to about $\frac{1}{6}$ the chromium by weight. Any places where the articles are not to be coated can be masked as by an intervening layer of nickel powder diluted with alumina.

A layer of aluminum can then be diffused in over the chromium-diffused case. This aluminum diffusion can be a simple pack aluminizing or can be the more complex aluminizing from packs that contain chromium as well as aluminum, such as shown in Canadian Pat. 806,618 or U.S. Pat. 3,257,230. Some of the chromium from such complex packs diffuses along with the aluminum into the surface being coated, but the extra chromium is not significant where that surface already contains a large content of chromium. For low temperature aluminizing, that is where aluminum diffusion is carried out at 1300° F. or below, more uniform coatings are obtained when nitrogen is excluded, as by using an activator such as aluminum chloride that does not liberate nitrogen. Manganese is a particularly desirable metal to add to an aluminum diffusion coating pack for coating ferrous metals such as stainless steels, and it provides a coating that is exceptionally protective against marine forms of corrosion, especially when such coating is covered by a conversion type coating.

Turning now to the drawings, the apparatus of FIG. 1 has been found very effective for diffusion coating in one step more than 40 milligrams chromium in each square centimeter of the surface of TD nickel jet engine burner rings, and to produce a high quality dense coated surface with very few or no inclusions. This apparatus has a bell-type furnace shell 10 placed around an outer retort 12 also of bell type and with its open bottom set on a sealing strip 14 over a retort base 16 embedded in a concrete floor 18. The outer rim 20 of the base is a water-cooling jacket to protect the sealing strip 14, and the center 22 of the base provides a bottom closure for the outer retort 12. Base center 22 has conduits 31, 32, 33 sealed through it for passing gas flushing lines 41, 42 as well as thermocouple leads 43, and can be made hollow so that it can be pressurized with gas and connected to a pressure gauge that indicates when any leak develops.

A well or hole 45 in floor 18 permits the passage of the gas lines and thermocouple leads to a location where they can be connected to gas supplies, valves, gauges and the like.

Above the retort base 16 there is placed a spacer 50 which can merely be in the form of a spider-like set of welded-together metal walls radiating from a center and spaced from each other to permit passage of the gas flushing and thermocouple lines. Above the spacer is mounted a plurality of inner retorts 51, 52 and 53 each in the form of an annulus with an open top 59. These inner retorts are shown as having cylindrical outer and

inner walls 61, 62 and an annular bottom sheet 63, the parts being dimensioned so that the jet engine deflector rings will be received in them. Such rings can have a wall thickness of about 40 mils with diameters of from about 10 to about 30 inches, and for such sizes the diameter of inner cylindrical wall 62 should be significantly less than 10 inches while the diameter of the outer cylindrical wall 61 should be significantly greater than 30 inches. The upper edges of these inner retorts have grooves or notches 67 that can act as vents, and the inside height of an inner retort between its floor 63 and the bottom of notches 67 is at least 15 inches, preferably at least 18 inches. It is also helpful to have a loosely fitted cover 71 over each inner retort.

A chromium diffusion operation is carried out by loading the inner retorts with the burner rings packed in a chromium diffusion pack such as one containing by weight 20% chromium powder, 3% nickel powder, 3% cobalt powder, 0.5% ammonium chloride powder, 0.05% magnesium chloride powder, the balance being alumina powder. The packed retorts are then stacked on the spacer 50, the outer retort 12 lowered over them, a stream of argon started through the flushing line 41, and the furnace shell 10 then placed around the assembly.

When the air in the retorts has been displaced by the argon the furnace is started and the flushing line 41 switched from an argon supply to a supply of dry hydrogen. The flushed gases exiting through line 42 can then be lit where they discharge from the exit conduit. The retorts are brought up by the furnace to 2100 to 2200° F. and kept therefor 20 to 30 hours under the control of one or more thermocouples. The heat is then shut off and the assembly permitted to cool. When the temperature in the inner retorts drops below 300° F. the hydrogen flush is replaced by an argon flush. After the hydrogen is flushed out the retorts can be opened and unloaded. The coated TD burner rings can then be given a light dry blast with 100 grit aluminum oxide at 20 pounds per square inch to clean up their surfaces, leaving them very smooth with a surface chromium content about 40% by weight and a chromium pick-up of about 50 milligrams per square centimeter of surface. No alpha chromium phase and no inclusions are present in the coating, and it is highly suited for receiving an aluminum diffusion coating.

The foregoing results are obtained with inner retorts 15 inches high. However when the heights of these retorts are ten inches and the process otherwise identical, the pick-up of chromium is only about half the foregoing amount. With retort cups deeper than 15 inches the chromium pick-up is slightly higher than with the 15 inch depths. The coating temperature should be at least 2150° F. to keep the coating time from being too long. After about 22 hours at 2150 to 2200° F. the coating rate diminishes sharply and further treatment tends to post-diffuse the deposited chromium rather than deposit significantly more chromium.

With the cobalt-nickel-chromium pack mixture the coating temperature need not be any higher than 2150° F. to obtain best results. When nickel is used in the pack without cobalt, it is preferred to have the coating carried out at 2200° F. Unless nickel is present in the pack in an amount about $\frac{1}{20}$ the weight of the chromium, the diffusion-coated case is apt to contain undesirable inclusions.

The presence in the coating pack of about 1 to 10% metallic iron by weight speeds up the chromium deposition, and permits the use of coating temperatures 25 to 100° F. lower than indicated in the above example. However the coating then tends to be somewhat rougher and also contain some inclusions. The iron can be added in the form of pure metal such as carbonyl deposited iron powder, or as ferrochrome or Ni-Fe or Cr-Ni-Fe alloy.

Varying the chromium content of the pack from about 5 to about 40% changes the surface chromium content

of the coatings but does not detract appreciably from the quality of the coatings. Varying the nickel content between about $\frac{1}{20}$ to about $\frac{1}{3}$ of the chromium by weight generally shows that the coating has fewest inclusions when the nickel content is between about $\frac{1}{10}$ to about $\frac{1}{4}$ of the chromium by weight. However better oxidation resistance and a faster coating rate is provided by the added presence of cobalt in an amount from about $\frac{1}{20}$ to about $\frac{1}{5}$ the weight of the chromium. Because of such faster coating the coating temperature can be 50° F. lower with the cobalt-containing packs than with corresponding cobalt-free packs. The alumina in the pack can be replaced by any other inert filler such as kaolin, magnesium oxide or Cr_2O_3 , and such fillers can be used singly or in any combination. The coating step can also be performed in other types of equipment, so long as the minimum retort height is observed.

TD Nichrome containing about 20% chromium, 2% ThO_2 , the balance nickel, can be similarly diffusion coated with chromium. Good results are obtained with the TD Nichrome when the chromium pick-up in the coating is only about 30 to about 40 milligrams per square centimeter. However the diffusion of chromium into the TD Nichrome is slower than in TD nickel so that about the same treating temperatures and times are used.

The ammonium chloride in the above example is an activator that greatly speeds up the coating operation. Any other activator such as ammonium iodide, ammonium bromide, ammonium fluoride, ammonium bifluoride, elemental iodine, elemental bromine, hydrogen bromide, or the higher aluminum halides (chloride, bromide and iodide) can be used individually or in any combination, and in concentrations from about 0.1% to about 1% by weight. With a pack that is not perfectly anhydrous, the minimum activator content should be $\frac{1}{4}$ %.

The magnesium chloride seems to improve the coating, possibly because it does a little scavenging of residual oxygen, and only about 0.01 to about 0.1% by weight is a suitable amount for this purpose. Magnesium iodide and/or magnesium bromide can be substituted for some or all of the magnesium chloride.

The pack, or at least those pack ingredients that remain solid during the coating, is of relatively fine particle size. The maximum particle size is desirably 150 microns and preferably less than 40 microns, although the activator and scavenger particles can be up to about 1 millimeter in size without detracting from the quality of the coating. Best results have been obtained with metal particles less than 10 microns in size and with filler particles up to about 40 microns in size.

The chromium diffusion packs also give better results for the second and subsequent coating treatments after they are freshly mixed. If desired the freshly mixed packs can be subjected to a blank run without workpieces before they are placed in service. Used packs are simply re-used with the addition of another charge of activator, and scavenger if desired, so long as the metal content is adequate. About 1 to 2% chromium can also be added to used packs to keep the metal content substantially unchanged through successive coating runs. Where cobalt is a pack ingredient substantial amounts are consumed by the coating and should be replaced as by adding $\frac{1}{4}$ to $\frac{1}{2}$ % after each coating run. Any nickel additions should be kept very low inasmuch as there is very little nickel consumed during the coating.

It is not necessary to use a hydrogen flush or hydrogen atmosphere during the diffusion. An argon flush maintained throughout the coating treatment also gives good results although it is more awkward to monitor the argon flow because it does not burn. Indeed no flush whatever is needed in which case the outer retort can be sealed against its cover as by a molten glass seal.

The foregoing chromium coating operation adds enough chromium to the workpiece surface to significantly increase its height. At locations such as attachment sites and the

5

like where the greatest dimensional accuracy is needed, the workpieces can be masked as by a layer or pocket of a mixture of equal parts by weight inert filler and nickel powder.

FIG. 2 illustrates one masking arrangement in the coating of jet burner nozzles 100 having threaded shanks 102 which are to remain uncoated. In an inner retort cup 104 there is placed a layer 106 of masking compound deep enough to receive the entire shank 102 of a nozzle. This layer can be a mixture of 10-60% nickel powder and 40 to 90% alumina or other inert filler, by weight. Over layer 106 another layer 108 of metal-free inert filler is placed, this being a thin layer to keep particles from sintering in a groove 103 in the nozzle side wall. Another thin layer 110 having a nickel-containing composition like that of layer 106 tops off the masking combination.

A group of nozzles 100 is first pressed with their threaded shanks down into the layer 106, layer 108 is sprinkled and rolled over the surface of layer 106 and then covered with layer 110 until the shanks are completely submerged, leaving the upper portions of the nozzles protruding up from layer 110. There is then poured in a layer 112 of diffusion coating material that completely covers the nozzle tops.

When the nozzles are TD nickel or TD Nichrome and a heavy diffusion coating of chromium is desired, the retort cup 104 should be at least 15 inches high or should be set into retort cups at least 15 inches high as explained above. With other materials or for lighter coatings the retort cup need only be shallow enough to hold a single layer of nozzles. Layer 108 of FIG. 2 is free of metal and used where the workpieces have recesses that might be difficult to clean up after the coating.

Where the nozzles are not subjected to an extremely high temperature, they need not be made of TD nickel or TD Nichrome, but they can be made of metals like the nickel-base or cobalt-base superalloys, such as for example Inconel 600. Such alloys are better masked by the use of the nickel aluminide or cobalt aluminide masking mixtures described in parent application Ser. No. 837,811 inasmuch as such masking mixtures do not have any tendency to structurally weaken the masked portions of the nozzle. These masking mixtures are also somewhat more effective masking materials if they have been used once or twice in a masking operation.

Even where the workpieces to be masked are nickel-base or cobalt-base superalloys, it is sometimes desirable to use a thin layer such as layer 110 of masking mixture containing only nickel and filler at the edge of the masked area adjacent the area to be coated. The diffusion coatings ordinarily applied have a substantial ability to "throw" a short distance and it only takes about a $\frac{1}{32}$ to about a $\frac{1}{16}$ inch layer of such nickel-filler mixture to provide a sharp coating boundary and keep the diffusion coating from "throwing" where it is not wanted. The nickel-filler layer might have a tendency to weaken the superalloy, but the extreme thinness of such a barrier layer minimizes the weakening effect.

After the heavy chromium coating described above has been completed and the workpiece surface thus coated cleaned up, the material is ready for the diffusion coating of aluminum. This is readily accomplished with an aluminum-containing pack such as a mixture of 50 to 98% alumina and 2 to 50% aluminum by weight, using a coating temperature of 800 to 1100° F. and a coating time of about four to fifteen hours. Such aluminizing is an alternative to the more complex aluminizing referred to above as described in Canadian Pat. 806,618 and U.S. Pat. 3,257,230. The more complex type of treatment is generally conducted at 1950° F. for about six hours.

A good form of simple aluminizing is accomplished with a pack consisting of 70% alumina and 30% aluminum, activated with $\frac{1}{2}$ % aluminum chloride, using a coating temperature of 1000° F. for six hours. There is no mini-

6

mum retort height preference for aluminizing, but the aluminizing can be carried out in the apparatus of FIG. 1 or in any other form of diffusion-coating apparatus.

The simple aluminizing described above does not produce a consistently uniform coating when an ammonium halide is used as the energizer and the material being coated contains about 50% or more iron. The lack of uniformity appears to be due to the presence of nitrogen in the retort atmosphere during the coating, and the resultant erratic formation of nitrides. The aluminum chloride energizer does a good job of flushing out residual air without introducing nitrogen, but other energizers such as elemental iodine and bromine, iodine trichloride or similar nitrogen-free halogen compounds including halides of silicon, columbium, titanium, boron, zirconium, hafnium, tantalum, chromium, molybdenum, tungsten, iridium, osmium, platinum, gallium, germanium, tin and phosphorus will do the same although they are not preferred. Whichever energizer is used is preferably in an amount from about 0.1 to about 1% of the pack weight.

In general the simple aluminizing as well as the more complex aluminizing are preferably used to cause an aluminum pick-up of about 1-10 milligrams per square centimeter of surface coated, giving a coating case about 0.1 to about 2 mils thick.

A diffusion aluminizing is also improved by incorporating with the aluminum about $\frac{1}{4}$ to $\frac{3}{4}$ metallic manganese calculated on the weight of the aluminum. Thus a diffusion coating pack of 60% alumina, 30% aluminum and 10% manganese will give at 800° F. over a period of four hours an aluminized coating on superalloys or even stainless steels that is somewhat more protective, particularly against marine-type corrosion. Type 410 stainless steel compressor blades for instance, given a 1 mil thick coating case of the foregoing aluminum-manganese type at temperatures from 800 to 1100, will withstand corrosion in salt air for a longer period than the compressor blades coated from a corresponding manganese-free pack.

A conversion coating applied over the manganese containing aluminum diffusion coating or the manganese-free aluminum coating, further increases corrosion resistance. A particularly effective conversion coating for this purpose is one that is made by dipping the aluminized compressor blade after glass blasting to clean the surface, into an aqueous solution of phosphoric acid and chromic acid containing per liter, about 5 to 100 grams phosphoric acid and about 1 to 25 grams chromic acid, removing the dipped blade and permitting the solution to drain, followed by calcining the blade with the residual coating solution at 800° F. for ten minutes. Conversion coatings rely on the presence of a little hexavalent chromium that can bleed out from the coating gradually over an extended period and any such conversion coating can be used if desired, to help resist marine corrosion. However conversion coatings such as described in U.S. Pat. 3,385,738 are not sufficiently protective at elevated temperatures, that is about 800° F. or higher. The chromic acid-phosphoric acid coating of the present invention is much better in this respect and provides protection at temperatures as high as 1200° F.

Best results on aluminized greek ascoloy are obtained with 10 grams CrO_3 and 57 grams orthophosphoric acid per liter, the calcining being at 600° F. In general calcining temperatures can vary from about 350° F. to about 1200° F., and should be long enough to cause the conversion coating to become almost completely (at least about 90%) insoluble in water.

Phosphorous acid and other phosphorus acids like pyrophosphoric acid can be substituted for part or all of the orthophosphoric acid without significantly lowering the effectiveness of the conversion coating. Conversion coating weights of from about 0.5 to about 25 milligrams per square foot are effective, although preferred coating weights are from about 2 to about 8 milligrams per

square foot. These greatly prolong the useful lives of jet engine compressor blades of martensitic stainless steels that have a simple aluminized case, particularly in the salty air of marine use. Other ferrous metals such as austenitic stainless steels and even low alloy and plain carbon steels that have aluminum diffusion cases are also made much more resistant to marine corrosion by the foregoing conversion coating. However with low alloy and plain carbon steels the resistance to marine corrosion is further increased if before the aluminizing the metal is given a chromium or mixed chromium-nickel diffusion case or even a chromium plating. In general it is preferred for the ferrous surface to contain at least 10% chromium before aluminizing, whether or not manganese is included in the aluminizing pack, but sharply improved results are obtained when as little as 1% chromium is present in the surface.

Applying diffusion coatings on some high strength metals like type 410 stainless steel can cause loss of strength, particularly if the coating is applied at 1600° F. or higher, and the coated material is slowly cooled down from such high temperature. The strength loss can be minimized by quenching the coated product or the retort containing it, after the high temperature coating step, or by subsequently heating the product to 1200° F. as for example after the conversion coating is applied, and then quenching it in water or oil.

It is generally difficult to get uniform wetting of an aluminized blade by the conversion coating solution. To avoid this difficulty the aluminized blade can first be treated with aqueous alkali that attacks the blade surface, turning it black. Such attack proceeds uniformly over the surface or can be prolonged until the entire surface is blackened, after which the entire surface is treated with aqueous nitric acid to remove at least some of the black, any remaining black then can be scrubbed off, but this scrubbing is not essential. The resulting surface with or without the scrubbing now wets quite uniformly so that very good and very uniform conversion coatings are then obtained. Any other type of aqueous coating mixtures as well as non-aqueous coating mixtures will be more uniformly received by aluminized ferrous metal that has been so pre-treated.

Very good blackening is rapidly effected when sodium hydroxide is the alkali and if it is in a 5% concentration by weight, although other strengths as well as other alkalis such as potassium hydroxide, calcium hydroxide and even sodium or potassium carbonate will also be effective. The blackening is accompanied by gas evolution, but the reaction with the alkali seems to stop after a few minutes, regardless of the treating temperature (4 to 8 minutes when the alkali is 5% aqueous NaOH and the treatment is at 90° F.), and it is accordingly not possible to overheat. The reactivity toward alkali is restored by the nitric acid treatment, and the alkali-nitric acid cycle can be repeated if desired. Indeed the cycle, which removes about 0.1 mil of metal, can be applied about five times without seriously detracting from the corrosion resistance although it is preferred to have no more than three such cycles. The nitric acid treatment also stops after a while so that it too cannot overheat. The nitric acid treatment can also be with any strength acid and at any temperature, although the greatest removal of the black color takes place at 100 to 140° F.

As pointed out above, it is not necessary to remove all of the black coating produced by the caustic. A nitric acid treatment which is at least about 15% of the maximum obtainable gives very good results. Very dilute solutions (i.e. 1%) of alkali or acid take a long time in acting and are preferably avoided.

First stage turbine vanes of cobalt-base or nickel-base superalloys that have been aluminized with either the complex or simple aluminizing, are also improved by heating in air at 2050 to 2100° F. until their surface is uniformly whitened, generally about 10 to 20 hours, then glass blast-

ing after cooling to remove the white skin (which appears to be aluminum oxide). The resulting vane looks very much like the untreated aluminized vane, except for a loss of some color where the vane is a cobalt-base superalloy like WI 52, but the aluminized case is much more adherent and much less subject to spalling and the like on handling.

A vane of WI 52 composition can also be improved by modifying the composition so that it contains about 0.1 to 1% lanthanum or yttrium. Thus the normal WI 52 composition is 21% chromium, 1.75% iron, 11% tungsten, 2% columbium and/or tantalum, 0.45% carbon, the balance being cobalt. Such a composition modified by the addition of 0.5% lanthanum has a better life at high operating temperatures, that is at 2050 to 2100° F., and will better withstand the above-described heat treatment. The lanthanum, or a corresponding addition of yttrium, seems to bind oxygen present in the metal and keeps it from migrating to hot spots where in the form of oxides it can cause loosening or protective coatings like diffusion cases.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed:

1. In the process of diffusion coating articles of nickel containing dispersed thoria and nickel alloys containing 20% chromium and dispersed thoria with a deep layer rich in chromium from a diffusion coating powder pack in which the articles are embedded, the improvement according to which the coating is effected with the pack held in an unsealed retort cup at least 15 inches high, and the pack contains about 5 to about 50% chromium as well as nickel in a proportion from about $\frac{1}{3}$ to about $\frac{1}{20}$ of the chromium.

2. The combination of claim 1 in which the pack contains 0.01 to 0.1% magnesium halide.

3. The combination of claim 1 in which all the pack ingredients that remain solid during the coating have particle sizes smaller than 150 microns.

4. The combination of claim 3 in which the metal ingredients of the pack have particle sizes smaller than 40 microns.

5. The combination of claim 3 in which the pack also contains cobalt in an amount from about $\frac{1}{20}$ to about $\frac{1}{5}$ the weight of the chromium.

6. In the process of protecting articles of nickel containing dispersed thoria by diffusion coating them with chromium and then with aluminum, the improvement according to which the chromium coating is applied as a single coating step in accordance with claim 1.

7. In the process of diffusion coating articles of nickel containing dispersed thoria and nickel alloys containing 20% chromium and dispersed thoria with a deep layer rich in chromium from a diffusion coating pack in which the articles are embedded, the improvement according to which the pack contains about 1 to about 10% iron and the coating temperature is below 2100° F.

8. The combination of claim 1 in which the diffusion coating pack also contains about 1 to about 10% iron and the coating temperature is below 2100° F.

9. The combination of claim 1 in which the pack also contains cobalt in an amount from about $\frac{1}{20}$ to about $\frac{1}{5}$ the weight of the chromium.

10. In the process of protecting articles of nickel containing dispersed thoria by diffusion coating them with chromium and then with aluminum, the improvement according to which the diffusion coating with chromium is effected with a pack containing about 5 to about 50% chromium, nickel in a proportion about $\frac{1}{3}$ to about $\frac{1}{20}$ of the chromium, and cobalt in a proportion about $\frac{1}{5}$ to about $\frac{1}{20}$ of the chromium.

11. In the process of protecting articles of nickel containing dispersed thoria by diffusion coating them with

chromium, the improvement according to which the diffusion coating with chromium is effected with a pack containing about 5 to about 50% chromium, nickel in a proportion about $\frac{1}{3}$ to about $\frac{1}{20}$ of the chromium, and cobalt in a proportion about $\frac{1}{5}$ to about $\frac{1}{20}$ of the chromium.

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U.S. Cl. X.R.

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