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METHOD OF FORMING CHROMIUM AND ALUMINUM DIFFUSION ALLOYS ON METAL PIECES
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Fig. 1.

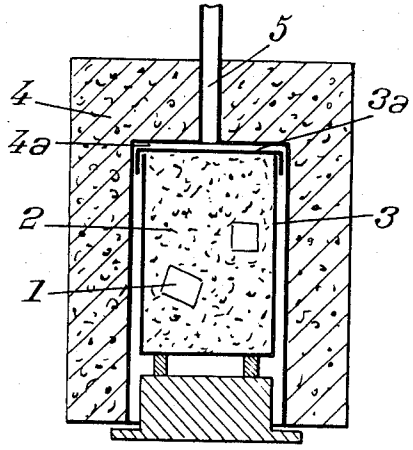
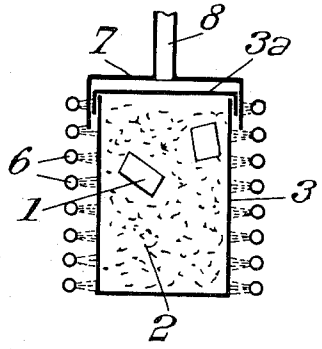


Fig. 2.



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3,690,934

METHOD OF FORMING CHROMIUM AND ALUMINUM DIFFUSION ALLOYS ON METAL PIECES

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Continuation-in-part of abandoned application Ser. No. 594,239, Nov. 14, 1966. This application July 1, 1970, Ser. No. 51,726

Int. Cl. C23c *11/00, 13/00, 17/02*

U.S. Cl. 117—107.2 P 19 Claims

ABSTRACT OF THE DISCLOSURE

The metal pieces to be treated are embedded in a reactive mass contained in a partly gastight box placed in a heating vessel wherein there is an at least partly hydrogenated protective atmosphere. The reactive mass comprises an intimate mixture of (1) a powder alloy of chromium and aluminum, (2) an inert powdered diluting component and (3) a halogen-containing component. The box and its contents are heated to 1050° C.–1100° C. for a few hours, then cooled. The starting chromium powder for the chromium-aluminum alloy powder may be of either magnesothermic or electrolytic origin and at least the electrolytic chromium is subjected to at least one pretreatment, prior to alloying, by exposure to either magnesium or calcium vapor to substantially reduce the amount of free oxygen on and in the chromium grains.

RELATED APPLICATION

This application is a continuation-in-part of our application Ser. No. 594,239, filed Nov. 14, 1966, now abandoned..

THE INVENTION

The present invention relates to methods of forming diffusion alloys of chromium and aluminum, and possibly silicon, on refractory and other metal pieces.

The chief object of the present invention is to provide a method of this kind which is better adapted to meet the requirements of practice than those known up to this time and in particular which results in pieces that have an increased resistance to corrosion, particularly to the corrosive action of combustion gases at high temperature.

The term "refractory metal piece" designates a piece made, either in its whole mass, or in the superficial portion thereof, chiefly (i.e. for at least 50% of its weight) of a material of the group consisting of iron, nickel, cobalt, tungsten, molybdenum and alloys of at least two of these metals, the whole of the component or components of this material being such, both from the point of view of its, or their, nature and from that of the respective proportions thereof if there are several components, that said material has, in the absence of any protective treatment, the capacity of resisting mechanical stresses in the hot state and furthermore, generally, some resistance to corrosive actions at high temperatures, in particular in oxidizing, oxido-reducing, or sulfurized atmospheres such for instance as those constituted by the combustion gases produced in internal combustion engines, especially gas turbines.

At the present time, such materials belong to four chief classes, to wit:

Stainless steels, among which may be cited, by way of example, "Inoxium" steel (Fe 83%, Cr 17%), 18–8 steel (Fe 74%, Cr 18%, Ni 8%) and 25–20 steel (Fe 55%, Cr 25%, Ni 20%);

Refractory steels, among which may be cited, by way of example, "Nickral-D" (Cr 25%, Ni 25%, C from 0.10% to 0.4%, the remainder Fe);

Nickel base refractory alloys, among which may be cited, by way of example,

"Nimonic 75" (Cr 20%, Ti 0.4%, Al 0.06%, Fe 2.4%, C 0.10%, the remainder Ni),

"Nimonic 80" (Cr 20%, Ti 2%, Al 2%, C 0.10%, the remainder Ni),

"IN 100" (Cr 9.5%, Mo 3%, Co 15%, Ti 5%, C 0.20%, Al 5.5%, W 1%, the remainder Ni),

"Inconel 713" (Co 10%, Cr 13.5%, Ti 2%, Al 5.5%, Mo 5%, Nb 2.5%, C 0.10, the remainder Ni),

"P.W.A. 663" (Co 10%, Cr 8%, Ti 1% Mo 6%, Ta 414%, the remainder Ni),

"TD Nickel" (Ni 98%, Th 2—2%);

And cobalt base refractory alloys, among which may be cited, by way of example, "HS 25," or "L 605" (Cr 20%, Ni 10%, W 15%, Fe 3%, C 0.10%, the remainder cobalt), "WI 52" (Cr 21%, W 11%, Nb and Ta 2%, Fe 2%, C 0.50%, the remainder cobalt) and "SM 302" (Cr 21%, W 10%, Ta 9%, Fe 1%, C 0.85%, the remainder cobalt).

It should be well understood that the above cited refractory materials may be obtained through various methods such as melting, sintering, electrodepositing, etc. and that they may contain, as in the above cited T. D. Nickel, a refractory component in the form of non coherent dispersed phase introduced in the form of particles during the preparation of said materials. The term "non coherent" means that this dispersed phase is of a crystalline structure different from that of the other components of said materials.

It should be noted that the invention also applies to the case where the above cited refractory metal pieces have undergone another superficial metal diffusion treatment, in particular a tantalum or chromium diffusion treatment.

The term "magnesothermic chromium" designates an ultrafine chromium powder obtained through a magnesothermic process. The production of such powders has been described in prior publications and in particular in the French Pat. No. 1,123,326 and in the French Addition Pats. No. 70,936 and 79,879 filed by the assignee of the present application. These French patents disclose a method of preparing chromium powder by reducing a chromium compound, especially a chromium oxide or halide, by a magnesium vapor.

More specifically a powder of chromium oxide Cr_2O_3 is placed in a container containing a protective gas, such as hydrogen, and also magnesium, but separated from the chromium oxide; a neutral compound, such as magnesium oxide, may be added to the chromium oxide. The container is heated to a temperature permitting the production of magnesium vapors which react with and reduce the chromium oxide producing chromium powder and magnesium oxide. The magnesium oxide (magnesia—MgO) may be removed by nitric acid.

Very fine chromium powder (having an average grain size of about 1 micron) may be obtained by this magnesothermic method.

Our invention consists, chiefly, in order to form on the surface of the refractory metal piece a diffusion alloy by addition of chromium and aluminum, and possibly of silicon;

In placing the piece to be treated in contact, over its whole surface, with a reactive mass comprising, inti-

mately mixed together, three kinds of chief components, to wit, firstly, a metal component in the form of an ultra-fine powder, of a mean grain size at most equal to one micron, every grain of which is made of an alloy consisting mainly of chromium and further comprising aluminum (in a proportion by weight ranging from 5 to 25%) and possibly silicon (in a proportion by weight ranging from 3 to 10%), said alloy powder being possibly formed either "in situ" by a preliminary thermal treatment performed before the introduction of the piece to be treated into the reactive mass, or at another place during a wholly independent operation, the formation of said alloy powder being preferably effected "in situ" from magnesothermic chromium and very fine aluminum powder made of particles at least one dimension of which is at most equal to one micron, secondly a component acting as diluting substance, inert from the chemical point of view, and in the form of a fine powder (of a grain size preferably of the order of magnitude of one micron), such a diluting substance consisting for instance of an oxide having a very high heat of formation, such for instance as calcined alumina and, thirdly, a liquid or divided halogen containing component of the group consisting of halogens, halides, hypohalogenites and mixtures of at least two of said bodies, the proportions by weight of these three components being preferably of from 5 to 50% for the metal component, from 0.05 to 1% for the halogen containing component, the remainder being the component acting as inert diluting substance;

In placing this reactive mass, with said refractory metal piece to be treated disposed inside said mass, in a partly gastight box, itself housed in a heating vessel wherein there is an at least partly hydrogenated protective atmosphere which may be constituted in particular by ordinary electrolytic hydrogen, a mixture of hydrogen and argon, or cracked ammonia;

In heating the whole, said heating vessel being kept at a temperature ranging from 750° C. to 1200° C., and preferably from 1050° C. to 1100° C., for a time ranging from a portion of one hour to some twenty hours, and preferably of the order of magnitude of a few hours, the temperature and duration of this heating being chosen, in particular, in accordane with the desired thickness of the layer of diffusion alloy;

And, finally, in cooling down said box in a protective atmosphere, which may be the same as that used during heating, this cooling step being advantageously conducted in such manner as to pass quickly through the temperature ranges (lower than 1000° C.).

It should be noted that if, according to the preferred form of the invention, the ultra-fine powder of chromium and aluminum alloy is formed "in situ" from magnesothermic chromium and aluminum powder, the reactive mass and the conditions of operations will be the same as those above set forth concerning the main feature of the invention, with the only difference that the piece to be treated will not have been placed inside said reactive mass in the partly gastight box.

It also has been discovered in accordance with this invention that electrolytic chromium powder having a mean grain size of from 1 to 20 microns may be used in place of the magnesothermic chromium powder provided that the electrolytic powder is first treated by exposure to magnesium and/or calcium vapor to substantially reduce any free oxygen in or on the powder, and to cause magnesium and/or calcium to be present in the powder. The results of such a substitution are satisfactory in the overall process but are not quite so good as when the 1 micron (ultra-fine) magnesothermic chromium powder is used.

It has been further discovered in accordance with this invention that the efficacy of the magnesothermic chromium powder is increased by treating it, prior to alloying, by exposure to magnesium and/or calcium vapor, although magnesium vapor is preferable. This substantially reduces the free oxygen that has been sorbed on or into the powder grains subsequent to the time of their initial manufacture and facilitates the diffusion of aluminum.

Therefore, an object of this invention is to provide a novel method for depositing chromium and aluminum alloys on refractory and other metal pieces in which the pieces to be treated are embedded in a reactive mass comprising an intimate mixture of (1) a powder alloy of chromium and aluminum, (2) an inert powdered diluting component and (3) a halogen-containing component, the reactive mass and its embedded contents being contained in a partly gastight box maintained in partly hydrogenated protective atmosphere and heated to about 1050° C.–1100° C. for a few hours and cooled.

Another object of this invention is to provide a method of the character stated in which the starting chromium powder for the chromium-aluminum alloy powder preferably is magnesothermic and having an initial mean grain size not greater than 1 micron.

Another object of this invention is to provide a method of the character stated in which the starting chromium powder for the chromium-aluminum alloy powder may be electrolytic having an initial mean grain size between 1 and 40 microns, preferably between 1 and 20 microns.

Another object of this invention is to provide a method of the character stated in which the starting chromium powder, whether magnesothermic or electrolytic, for the chromium-aluminum alloy powder is subjected to at least one pretreatment prior to alloying by exposure to magnesium and/or calcium vapor to substantially reduce the amount of free oxygen on and in the chromium grains and thus create superior operating conditions for the formation of the alloy powder and the subsequent chrome-aluminization diffusion coating of the metal pieces when embedded in the reactive mass containing the alloy powder.

A further object of this invention is to provide a method of the character stated in which the chromium-aluminum alloy powder is treated by exposure to magnesium and/or calcium vapor prior to becoming admixed into the reactive mass.

A further object of this invention is to provide a novel chromium-aluminum alloy powder in which the chromium, prior to alloying, has been treated by exposure to magnesium and/or calcium vapor.

A further object of this invention is to provide a novel reactive mass for forming a diffusion alloy of chromium and aluminum on a metal piece.

Preferred embodiments of our invention will be hereinafter described with reference to the appended drawings, given merely by way of example, and in which:

FIGS. 1 and 2 diagrammatically illustrate apparatus for carrying out the method according to the present invention, FIG. 1 corresponding to the chrome-aluminization thermal treatment proper, whereas FIG. 2 corresponds to a cooling operation following said thermal treatment.

In FIG. 1, the pieces 1 to be treated are embedded in the reactive mass 2 contained in a steel box 3 having a partly gastight cover 3*a*, said box 3 being disposed in the chamber 4*a* of a bell-shaped furnace 4, an at least partly hydrogenated protective atmosphere being fed through a conduit 5 into said furnace.

It will be of interest to dispose several independent treatment boxes such as 3 in chamber 4*a*, these boxes being then advantageously separated from one another by cross members which permit a quick and more uniform heating of the reactive masses.

FIG. 2 illustrates the cooling of box 3 after the thermal treatment by means of water spraying means 6 after box 3 has been quickly conveyed under protective cover 7 fed with an at least partly hydrogenated protective atmosphere through a conduit 8. The suction produced in box 3 by the cooling thereof facilitates the inflow of the protective atmosphere into said box.

Attention is called to the essential importance of the ultra-fine character of the metal component of the reac-

tive mass (alloy powder having a grain size of at most one micron).

Such an ultra-fine grain size of the alloy powder not only ensures a great surface area, which is of course favorable to exchange reactions, but also ensures an advantage of essential importance when, as in the present case, the alloy powder contains aluminum.

As a matter of fact, aluminum conveyed from the superficial layer of every alloy powder grain to the surface of the piece to be treated has a tendency to diffuse more quickly in the crystalline network of the treated piece than in the crystalline network of the grain that is considered. This therefore causes a loss of aluminum in the superficial layer of the grains, which corresponds, by a compensating effect, with a transfer of aluminum atoms from the heart of the alloy grains to the surface thereof. Now, the effects of this transfer are felt the more quickly as the path of travel of the aluminum atoms is shorter. It will be understood that, in these conditions, it is of very great interest, in a method according to the invention, to give the alloy powder an ultra-fine character due to the fact that the superficial layer of every grain will be quickly regenerated in aluminum from the inside of the grain due to the very short distance said aluminum has to travel over, which keeps to a constant value the aluminum to chromium ratio of the alloy deposited.

It should be noted that the preferential transfer of aluminum to the treated piece (due to the higher electropositivity of this metal) may be easily compensated for by adding a small amount of aluminum powder into the reactive mass between every two successive treatment operations. For instance, this addition of aluminum powder may be of from 0.5 to 1% by weight of said reactive mass. Furthermore, also between every two successive treatment operations, an addition of the halogen containing component snould be made, in the amount of from 0.05 to 1% by weight of the reactive mass.

As for the gradual, but slower, consumption of the chromium of the reactive mass, it may be compensated for by adding to said mass from time to time, for instance on every fourth or fifth operation, a small amount of ultra-fine chromium powder, at the rate also of from 0.5 to 1%.

The ultra-fine grain size of the metal component of the reactive mass implies a fine grain size of the component acting as inert diluting substance. It has been above stated that this small grain size is preferably of the order of magnitude of one micron. But this is not an imperative condition since the small grain size of the component acting as inert diluting substance is less essential than that of the metal component. For instance we may use an inert diluting substance of a grain size lower than one micron or on the contrary an inert diluting substance of a grain size greater than one micron, the proportion of inert diluting substance being higher in this last mentioned case.

It should also be noted that the ratio of the weight of inert diluting substance to the weight of metal component in the reactive mass has not a critical character. For practical purposes this ratio may range from 1 to 20.

In addition to the above stated advantages, we may also cite the following ones:

Concerning the treated pieces, the obtainment of a gastight outer sheet free from porosity and cracks, the excellent surface state of said pieces, the plasticity of the surface layers both in the cold and in the hot state (which plasticity gives the pieces an exceptional resistance to thermal shocks), and an increased percentage of chromium in said superficial layer, giving in particular the pieces a better behavior in sulfur containing combustion gases;

Concerning the reactive masses, the fact that said masses do not undergo any "ageing" and do not suffer from any inhibition (the percentage of nitrogen therein may without danger reach high values), which permits a practically unlimited duration of use of said masses, and also the fact that these reactive masses never comprise brittle and uneasily dissociable intermetallic compounds of chromium and aluminum.

It should be well understood that the method according to the present invention may be applied in a single operation or in two or several successive operations without it being necessary to proceed with intermediate treatments such as scouring or sanding. The method according to the invention may also be used for restoring pieces that have already been used. In this case, it is necessary to proceed with a preliminary elimination of the oxide layer, by intensive sanding or chemical attack.

We will now give some examples in which the method according to the present invention is applied to various refractory alloys, the reactive mass used in these examples having the following composition, the character of which is not limitative and may vary within a rather wide range provided that the conditions above stated when defining the invention are complied with:

	Percent by weight
Magnesothermic chromium in ultra-fine powder	40
Very fine aluminum powder	10
Fine calcined alumina	49.2
Ammonium chloride (or bromide)	0.8

It should be noted that it may be advantageous, if the materials to be treated are strongly carburized, to add to said reactive mass, in addition to ammonium chloride (or bromide), about from 0.5 to 1% by weight of a compound such as aluminum fluoride (AlF_3,, 0.5 H_2O or AlF_3, 3.5 H_2O), this compound acting as superficial decarburizing substance at the beginning of the operation.

This reactive mass is used in the following Examples 1 to 7 and the chromium-aluminum alloy is formed "in situ" in a preliminary operation, i.e. without the presence of the piece to be treated conducted at 1000–1100° C. for at least one hour, the other above-mentioned conditions for the treatment, according to the invention, being complied with.

EXAMPLE 1

Protection of moving turbine blades in a gas-turbine

The pieces to be protected, made of the refractory alloy "Inconel 713," are subjected to a treatment, as above stated, for six hours at a temperature of 1080° C.

After the treatment, the pieces have a very smooth surface and a very homogeneous semi-bright sky blue appearance. The thickness of the diffusion layers that are obtained reaches about 65 microns. These protective layers, rich in chromium and aluminum, are free from any porosity, inclusion or crack. They are quite plastic, even in the cold state, whatever be the rate of deformation applied to the pieces. Furthermore they are not affected by the most violent thermal or mechanical shocks.

Corrosion resistance tests in combustion gases, even containing a high proportion of sulfur, conducted for 300 hours at 1100° C. with thermal shocks at time intervals, have made it possible to observe that the rates of scaling measured at the end of the tests are practically negligible (lower than 2 mg./cm.^{2}), whereas the same pieces subjected to similar tests without having been treated to ensure a preliminary protection are seriously damaged and have scaling rates as high as from 30 to 40 mg./cm.^{2}.

Substantially equivalent results concerning the appearance of the pieces, the homogeneity and plasticity of the surface layers, the resistance to corrosion and thermal shocks have been obtained by treating in the same conditions pieces constituted by other refractory alloys of tne nickel base type such as "SM 200," "Udimet 700," "P.W.A. 663," "IN 100" and "T.D. Nickel."

In these cases also the rates of scaling observed after corrosion tests in high temperature combustion gases are practically negligible for pieces protected according to the invention, whereas the rates of scaling observed with the

same materials but without preliminary protection are generally very high and may, in some cases ("T.D. Nickel," "IN 100"), correspond to complete destruction of the pieces.

EXAMPLE 2

In this example, the pieces to be protected are the same as in Example 1 but the treatment is performed for 20 hours at 900° C.

The surface appearance characteristics, the homogeneity of the chromium and aluminum diffusion layers, the plasticity either in the cold or in the hot state, the resistance to thermal shocks, are analogous to the characteristics described in Example 1, but the thickness of the diffusion layers is smaller and range from 25 to 35 microns approximately, according to the nature of the materials that are treated.

EXAMPLE 3

In this example, the conditions of treatment and the materials that are treated are the same as in Example 1, but the roots of the blades are initially coated with several thicknesses of iron or nickel cloth and are placed in cups containing powdered calcined alumina, possibly with the addition of iron powder or nickel powder. The cups that contain alumina are machined so as to fit nearly exactly on the rectangular upper portion of the blade roots.

The thickness of the layers obtained on the surfaces that have not been thus shielded is not influenced by the modification made in the conditions in which the treatment is carried out. By contrast, the shielded blade roots are practically not chrome-aluminized.

EXAMPLE 4

Protection of turbine distributing blades made of the cobalt base refractory alloy "HS 25"

The pieces to be protected are treated for 8 hours at a temperature of 1080° C.

After the treatment the pieces have a very smooth superficial state and a very homogeneous semi-bright light orange beige appearance. The thickness of the diffusion layers reaches 55 microns approximately. These protective layers rich in chromium and in aluminum are free from any porosity, inclusion or crack. They are quite plastic even in the cold state, whatever be the rate of deformation applied to the pieces and are not sensitive to the most violent mechanical or thermal shocks.

Corrosion tests in high temperature combustion gases, analogous to the test described with reference to Example 1, prove that the application of the treatment according to the present invention to such materials made it possible to reduce by more than 95% the rate of scaling observed in pieces subjected without preliminary protection to these tests.

EXAMPLE 5

Protection of turbine distributing blades made of cobalt base carburized refractory alloys "WI 52"

The pieces to be protected are subjected to a treatment of 10 hours at a temperature of 1050° C.

After the treatment, the pieces have a very smooth surface condition and a light orange beige appearance.

The thickness of the diffusion chromium and aluminum layers reaches about 45 microns, these layers being free from any porosity, inclusion or crack and being not affected by the most violent mechanical or thermal shocks.

Corrosion tests in high temperature combustion gases analogous to those described in Example 1 show that the treatment according to the invention reduces by more than 97% the rate of scaling observed normally on pieces that have not been protected.

The treatment just above mentioned may also be carried out in two successive operations at a temperature of 1075° C., each of a duration of 10 hours.

In this case, the thickness of the protective layers reaches 60 microns.

EXAMPLE 6

Protection of combustion chambers consisting of brazed assemblies of 18/8 stainless steel "Nimonic 75" and "HS 25"

The pieces are constituted by assemblies of 18/8 stainless steel (roots), "Nimonic 75" (combustion chambers proper) and "HS 25" (flame tubes) preliminarily brazed under a vacuum by means of nickel-chromium-boron-silicon brazings.

The pieces to be protected are subjected to treatment for 15 hours at 980° C. After the treatment, the thickness of the chromium and aluminum diffusion layers reaches 120 microns on the 18/8 stainless steel portions, 50 microns on the "Nimonic 75" portions and 40 microns on the "HS 25" portions, these layers being in all cases free from any inclusion, porosity or crack and substantially plastic both in the cold and in the hot state.

During trials and utilization tests on engines, performed in particularly hard conditions, no failure of the layers was observed in the case of fuels containing a high percentage of sulfur. The rate of scaling of the treated pieces remains in all cases practically negligible.

EXAMPLE 7

Protection of turbine moving blades of "Inconel 713" preliminarily provided with protective layers of diffusion of tantalum

Before the treatment according to the present invention the blades were covered with protective layers by diffusion of tantalum, this preliminary treatment making it possible substantially to improve the characteristics of resistance to scaling of the materials under treatment.

In order to perform this preliminary tantalizing treatment, the pieces were heated, for 4½ hours, at 1080° C. in partly gas-tight boxes placed in a hydrogenated protective atmosphere, said boxes being embedded in a powdery mixture consisting of fine calcined alumina (97.5% by weight) and very fine tantalum powder (2.5% by weight), with the addition of 0.5% by weight of ammonium chloride.

This preliminary treatment led to the obtainment of diffusion layers very rich in tantalum and of a thickness of 30 microns, with preferential deeper penetration of tantalum along the grain joints of the material.

The preliminarily tantalized "Inconel 713" blades were subjected to a treatment according to the invention in a chrome-aluminizing mass containing an addition of 5% of silicon and preliminarily homogenized in an operation conducted in the absence of the treated pieces. The protection treatment lasted 8 hours at a temperature of 1080° C.

After the protection treatment by simultaneous diffusion of aluminum, chromium and silicon, the pieces have a very smooth surface condition and a very homogeneous semi-bright sky blue appearance. The protective diffusion layers that are obtained have a thickness of about 55–60 microns. They are free from any porosity, crack or inclusion and quite plastic, even in the cold state. They ensure an excellent protection of the treated pieces for very long times, against the action of combustion gases, up to temperatures as high as 1100° C.

EXAMPLE 8

Chrome-aluminizing of "T.D. Nickel" pieces, preliminarily treated by diffusion of tantalum on the surface thereof

The pieces to be protected are pieces for experimental turbine wheels. They have undergone a preliminary coating treatment by diffusion of tantalum. This preliminary treatment is intended to avoid too deep a rediffusion of aluminum during the utilization of the protected pieces. It also permits a reaction to be avoided between the

thoria of the "T.D. Nickel" and the aluminum added in the nascent state during the chrome-aluminizing treatment.

Thoria can also be eliminated from the superficial layers of the pieces in the following manner. The pieces are placed in partly gastight containers in the presence of ammonium fluoride, either acid or neutral, and of metal in the divided state (nickel in the present case). The whole is heated in a hydrogenated protective atmosphere. A treatment of about 1 hour at a temperature of 1050–1100° C. is sufficient in the present case in which the thoria is dispersed in the pieces.

The pieces thus obtained have a homogeneous semi-bright surface appearance. The protective layers formed as a consequence of the superposition of the two successive treatments are plastic in the cold state and of a regular thickness equal to about 50 microns. They ensure a particularly efficient protection of the treated pieces against the corrosive action of the high temperature combustion gases, even in the case of very severe thermal shocks.

EXAMPLE 9

Chrome-aluminizing of "T.D. Nickel" pieces which have not undergone a preliminary tantalum diffusion treatment

The chrome-aluminizing treatment is the same as in the preceding example, but, prior to this treatment, the superficial layers of the ipeces are deoxidized by a treatment of 1 hour at 1100° C. in a fluorine container atmosphere (heating of the pieces placed in nickel grids inside partly gastight boxes containing acid ammonium fluoride in the amount of two grams per liter and chromium in grains disposed at the bottom of the boxes, out of contact with the pieces).

Pieces thus treated have a uniformly bright appearance and their superficial layers are practically free from thoria over a depth of about 100 microns.

After the chrome-aluminizing treatment that follows, the pieces obtained have a semi-bright appearance and are coated with chromium-aluminum diffusion alloys which are distinctly plastic even in the cold state, free from cracks or inclusions and the thickness of which reaches about 65 microns.

EXAMPLE 10

Chrome-aluminizing of "Inconel 3" refractory alloy pieces preliminarily coated by diffusion of chromium

In the case of this example, the preliminary coating treatment by diffusion of chromium is intended, on the one hand, to ensure an improved behavior of the protected pieces in combustion gases containing a high proportion of sulfides and, on the other hand, to reduce the intergranular penetration of aluminum which may occur in the superficial areas of the pieces when the chrome-aluminizing treatment is performed.

The preliminary chromizing treatment is performed in conditions which avoid the formation of superficial areas made brittle by too rich an inclusion of chromium. The pieces are chromized by means of a treatment mass bringing into play ultra-fine powders of nickel and chromium obtained by preliminary heating of a mixture of magnesothermic chromium ultra-fine powder (25% by weight), of fine nickel powder (10% by weight) and of fine calcined alumina (65% by weight), with the addition of 1% by weight of ammonium chloride. The chromizing reactive masses thus formed are maintained to the desired composition by the addition, between successive operations, of 1% by weight of chromium powder and of 0.5% of ammonium chloride or bromide. In the case that is considered, the pieces undergo a chromizing heating of 6 hours at 1050° C. under a protective atmosphere of hydrogen.

This treatment causes the formation of chromium diffusion layers which are smooth and of a homogeneous semi-bright appearance, plastic in the cold state due to the limited contents of chromium, these layers having a regular thickness equal to about 35 microns.

The pieces thus chromized then undergo a plastic chrome-aluminization treatment in the same conditions as those described in the preceding example. The pieces then have a homogeneous semibright surface appearance and are coated with diffusion alloys, rich both in chromium and in aluminum, the total thickness of which reaches about 65 microns. These layers are plastic both in the cold and in the hot state and they ensure a very efficient protection of the pieces up to 1050° C. approximately in the combustion gases of fuels containing an amount of sulfur as high as 3 or 4%.

As previously noted, the efficacy of the method of this invention is enhanced and a superior end product results if the starting chromium powder for the chromium-aluminum alloy powder is first exposed to the vapor of magnesium and/or calcium (preferably magnesium) in order to substantially reduce the amount of free oxygen on the grains of chromium. Some of the magnesium or calcium remains in the chromium and serves to reduce the amount of free oxygen that subsequently may be attached to the chromium due to handling and to any time lag or delay that may occur in forming the alloy powder. The remaining Mg or Ca facilitates the diffusion of Al.

This preliminary treatment of the starting powder is effected at a temperature ranging from about 700° C. to upwards of 1200° C. for magnesium vapor preferably between 1000° C. and 1100° C. and at least 1000° C. for calcium vapor.

The following examples and tests clearly indicate the value of this preliminary treatment of the starting chromium powder. In each example strips of "Hastelloy X" and "Nimonic 75," having a thickness of 1 mm., were diffusion coated in accordance with this invention and tested.

EXAMPLE 11

(A) Preliminary treatment of starting chromium powder

In this example the starting material is a half product of chromium and magnesia (Cr+MgO) obtained by the magnesothermic reduction of chromium oxide (Cr_2O_3) by the method of the above mentioned French patents and has a composition approximating chromium 46% and magnesia 54%. A mixture of 1000 grams of this half product, 16 grams of magnesium chips or turnings and 4 grams of NH_4Cl was heated at 1080° C. for 2 hours in a chromide iron vessel under a hydrogenated atmosphere. After cooling, it was washed with diluted nitric acid and then with distilled water to remove the magnesia (MgO). It was dried and the resulting chromium powder had the following characteristics:

	Before treatment	After treatment
Grain size, microns	1	1.2
Cr_2O_3, percent	0.9	0.0
Total oxygen, percent	0.6	0.3
Magnesium, percent	0.18	0.25

(B) Preparation of chromium-aluminum alloy powder

A mixture of 450 grams chromium powder from step A, 100 grams ultra-fine aluminum powder (Merck), 450 grams fine alumina (precalcined 4 hours at 1080° C.) and 5 grams NH_4Cl was prepared and heated in a hydrogenated atmosphere for 14 hours at 1080° C. to produce the desired alloy powder.

(C) Diffusion coating of test pieces

The test pieces were embedded in the reactive mass (as hereinbefore described) at 600° C., then raised to 800° C. in 30 minutes, then to 1065° C. in 2 hours and held there

for 5 hours and 30 minutes, after which cooling was effected over a period of 2 hours.

(D) Tests

(1) Electronic scanning indicates enrichment of the surfaces of the test pieces in chromium.

(2) Concentration of chromium peaks beneath the layer that originally was aluminum.

(3) Bending 180° around a 17 mm. diameter mandrel did not produce any cracks or fissures.

(4) A repeated cyclic heating and cooling, through 300 cycles, by bringing the samples to 1100° C. in two (2) minutes, then holding that temperature for one half hour and cooling in a draft of air for 30 seconds, did not produce any scaling.

(5) Excellent corrosion tests at a constant temperature.

(6) Also excellent corrosion tests on 180° bent pieces.

EXAMPLE 12

(A) Preliminary treatment of starting chromium powder

This is the same as in Example 11, except that the NH_4Cl is eliminated and the gaseous heating atmosphere is argon. The resulting chromium powder had the following characteristics:

	Before treatment	After treatment
Grain size, microns	1	1.2
Cr_2O_3, percent	0.9	0.1
Total oxygen, percent	0.6	0.35
Magnesium, percent	0.18	0.20

(B) Preparation of chromium-aluminum alloy powder

The same as in Example 11.

(C) Diffusion coating of test pieces

The same as in Example 11.

(D) Tests

Nearly as good as tests 1–6 in Example 11.

EXAMPLE 13

(A) Preliminary treatment of starting chromium powder

In this example the starting material is an electrolytic chromium powder having a mean grain size between 10 and 40 microns with an average grain size of 20 microns. A mixture of 500 grams of this chromium powder, 250 grams magnesia, 2.5 grams bromine, 2.5 grams iodine and 12 grams magnesium chips or turnings was processed as in Example 11 and the resulting chromium powder had the following characteristics:

	Before treatment	After treatment
Grain size, microns	10–40	(1)
Cr_2O_3, percent	0.0	0.0
Total oxygen, percent	0.43	0.1
Magnesium, percent	0	0.25

[1] No change, but rounder grains.

(B) Preparation of chromium-aluminum alloy powder

The same as in Example 11.

(C) Diffusion coating of test pieces

The same as in Example 11.

(D) Tests

(1) No chromium enrichment of the surfaces was observed in any substantial degree.

(2) The 180° bending about the 17 mm. diameter mandrel is satisfactory but not as good as in Example 11.

(3) There is very slight scaling at 300 cyclic thermal operations.

EXAMPLE 14

This is the same as Example 13 except that in step A the 12 grams of magnesium are replaced by 20 grams of calcium. The resulting chromium powder had the following characteristics:

	Before treatment	After treatment
Grain size, microns	10–40	(1)
Cr_2O_3, percent	0.0	0.0
Total oxygen, percent	0.43	0.15
Calcium, percent	0.0	0.12

[1] No change, but rounded grains.

The steps B and C were the same as in Example 11 and the test results under step D were slightly inferior, thus indicating that magnesium is to be preferred over calcium in the preliminary vapor treatment of the starting material.

EXAMPLE 15

In this example the starting material is an electrolytic chromium powder having a mean grain size of 1 micron, thus providing a comparison with magnesothermic powder of comparable grain size. The starting mixture comprises 500 grams chromium, 250 grams magnesia, 5 grams NH_4Cl and 50 grams of magnesium in chips or turnings. It is processed as in Example 11 and the resulting chromium powder has the following characteristics:

	Before treatment	After treatment
Grain size, micron	1	1.2
Cr_2O_3, percent	0.0	0.0
Total oxygen, percent	5.0	0.3
Magnesium, percent	0.0	0.25

Comparing the starting materials in Examples 13, 14 and 15, there appears to be a drastic increase in oxygen as the grain size is reduced. To state it another way, the amount of free oxygen on the grains of chromium before treatment is inversely proportional to the grain size; i.e., the smaller the grain size, the greater the total absorbing area exposed to free oxygen. Therefore, the treatment by magnesium and/or calcium has a more dramatic effect on oxygen reduction on smaller electrolytic grain sizes.

Steps B and C were the same as in Example 11 and the test results under step D were slightly inferior, thus indicating that the use of magnesothermic chromium powder is preferable to electrolytic chromium powder in this grain size.

EXAMPLE 16

Here the starting material is an electrolytic chromium powder of a grain size mixture extending from 1 to 10 microns. It is incorporated in a mixture of 500 grams chromium, 250 grams magnesia, 5 grams NH_4Cl and 30 grams magnesium chips or turnings and processed as in Example 11. The resulting chromium powder has the following characteristics:

	Before treatment	After treatment
Grain size, microns	1–10	(1)
Cr_2O_3, percent	0.0	0.0
Total oxygen, percent	1.3	0.3
Magnesium, percent	0.0	0.2

[1] No change.

Steps B and C were the same as in Example 11 and the test results under step D were intermediate between those of Examples 13 and 15.

For the purposes of comparison the following examples are included to show what happens if the starting chromium powder is not subjected to the preliminary treatment with magnesium or calcium vapor.

EXAMPLE 17

This example compares with Example 13. Step A was omitted and steps B and C were unchanged. The tests under step D indicate that:

(1) The diffusion layer is irregular, contains cracks and pores and shows no enrichment in chromium.

(2) There is a high content of aluminum on the surface and ther is no global addition of chromium.

(3) There are fissures and cracks at a bend of only 20° to 30° on the mandrel as compared with no fissures or cracks at an 180° bend in Example 13.

(4) In a constant temperature corrosion test, rediffusion of aluminum takes place in the course of time.

(5) Under thermal cycling scaling takes place after 10 cycles compared with 300 cycles without scaling in Example 13.

EXAMPLE 18

This example compares with Example 15. Step A was omitted and steps B and C were unchanged. The tests under step D indicate that:

(1) X-ray analysis shows the presence of the undesirable Cr_2Al intermetallic compound.

(2) The remaining results are comparable to those of Example 17 and are unsatisfactory.

It seems more generally that the treatment of the chromium powder by Mg and/or Ca vapor prevents the formation of detrimental intermetallic Cr_2Al compound in the alloy and inserts Mg and/or Ca in the chromium powder and later in the alloy, thereby eliminating the harmful free oxygen and facilitating the diffusion of aluminum.

Finally, a last example is included, wherein step B is different from step B of Examples 11 and 18.

EXAMPLE 19

(A) Preliminary treatment of starting chromium powder

The starting material is constituted by an electrolytic chromium having a grain size between 1 and 10 microns, as in Example 16.

A mixture of 500 grams of this electrolytic chromium, 500 grams of calcined alumina, 5 grams of NH_4Cl and 30 grams of magnesium chips or turnings was heated in hydrogen for two hours at 1080° C.

The diluent (alumina) was not eliminated at the end of step A and therefore the powder was not examined at the end of this step.

(B) Preparation of chromium and aluminum alloy powder

A mixture of 1000 grams of the product of step A, 109 grams ultra-fine aluminum powder (Merck) and 5 grams NH_4Cl was prepared and heated in hydrogen for 14 hours at 1080° C. to produce the desired alloy powder.

(C) Diffusion coating of test pieces

The same as in Example 11.

(D) Tests

Similar to the tests of Example 16, but very slightly not so good as in said Example 16.

In a general manner, while we have in the above description disclosed what we deem to be practical and efficient embodiments of the present invention, it should be well understood that we do not wish to be limited thereto as there might be changes made in the arrangement, disposition and form of the parts without departing from the principle of the present invention as comprehended within the scope of the appended claims.

We claim:

1. The method of forming a diffusion alloy of chromium and aluminum on a refractory metal piece made, at least in the superficial portion thereof, of at least 50% by weight of a material of the group consisting of iron, nickel, cobalt, tungsten, molybdenum and alloys of at least two of said group thereof which method includes:

forming an intimate mixture of, first an ultra-fine magnesium or calcium vapor-treated chromium powder having a mean grain size not substantially greater than twenty microns, secondly an aluminum powder in an amount ranging from 5 to 25% by weight of the chromium-aluminum portion of said intimate mixture, thirdly a powdered chemically inert diluting component consisting of an oxide which does not appreciably decompose at temperatures ranging from 750° to 1200° C. and, fourthly a halogen containing component of the group consisting of halogen, halides, hypohalogenites and the mixtures of at least two of said group thereof;

placing the whole of said mixture in a partly gastight box and placing said box in a heating vessel wherein there is an at least partly hydrogenated protective atmosphere;

heating said vessel and its contents at a temperature ranging from 750° to 1200° C. for a time ranging from a portion of one hour to some twenty hours;

cooling said box and its contents in a protective non-oxidizing atmosphere;

incorporating the powder of the alloy of chromium and aluminum that has been thus formed into a reactive mass comprising the three following components intimately mixed together first said alloy powder, secondly a chemically inert powdered diluting component consisting of an oxide which does not appreciably decompose at a temperature ranging from 750° to 1200° C. and, thirdly a halogen containing component of the group consisting of halogens, halides, hypohalogenites and the mixtures of at least two of said group thereof;

embedding said refractory metal piece in said reactive mass;

placing the whole of said reactive mass and said embedded refractory metal piece in a partly gastight box and placing said box in a heating vessel wherein there is an at least partly hydrogenated atmosphere;

heating said vessel at a temperature ranging from 750° to 1200° C. for a time ranging from a portion of one hour to some twenty hours, and

cooling said box and its contents in a protective non-oxidizing atmosphere.

2. A method according to claim 1 wherein said intimate mixture further comprises silicon powder in an amount ranging from 3 to 10% by weight of the chromium-aluminum portion of said intimate mixture.

3. The method according to claim 1 wherein said inert diluting component consists of calcined alumina.

4. The method according to claim 1 wherein the proportions by weight of the three components of the reactive mass are from 5 to 50% for the alloy, 0.05 to 1% for the halogen containing component, the remainder consisting of the inert diluting component.

5. The method according to claim 1 wherein said heating steps take place at a temperature ranging from 1050 to 1100° C.

6. The method according to claim 1 wherein said heating steps take place for from two to ten hours.

7. The method according to claim 1 wherein the protective atmosphere in which said box is cooled in each cooling step is the same as the protective atmosphere in which the previous heating step has taken place.

8. The method of claim 1 additionally including the steps of, removing said refractory metal piece after said box has been cooled, adding to said reactive mass, by weight, from 0.5 to 1.0% of aluminum powder and from 0.05 to 1.0% of the halogen containing component, replacing said removed refractory metal piece with a different refractory metal piece, and repeating all of said operational steps.

9. The method of claim 8 which, after having been repeated at least twice, each time with a different refractory metal piece, additionally includes the steps of adding to said reactive mass, by weight, of from 0.5% to 1.0% of ultra-fine chromium powder, replacing the last said removed refractory metal piece with a different

refractory metal piece, and repeating all of said operational steps.

10. A metal article comprising a refractory metal piece enclosed by a diffused outer layer formed by the method of claim 1.

11. The method of forming a diffusion alloy of chromium and aluminum on a refractory metal piece made, at least in the superficial portion thereof, of at least 50% by weight of a material of the group consisting of iron, nickel, cobalt, molybdenum, and alloys of at least two of said last mentioned metals, which method comprises:

placing the refractory metal piece in contact, over its whole surface, with a reactive mass comprising the three following components intimately mixed together, firstly an ultra-fine powder, of a mean grain size at most equal to 20 microns, every grain of said ultra-fine powder being made of an alloy consisting mainly of magnesium or calcium vapor-treated chromium and further comprising aluminum in a proportion by weight in the range of 5 to 25%, secondly a chemically inert powdered diluting component consisting of an oxide which does not appreciably decompose at temperatures in the range of 750 to 1200° C., and thirdly, a halogen containing component of the group consisting of halogens, halides, hypohalogenites and mixtures of at least two of said group thereof,

placing the whole of said reactive mass and said refractory piece embedded therein in a partly gastight box and placing said box in a heating vessel wherein there is an at least partly hydrogenated protective atmosphere,

heating said vessel to a temperature in the range of 750 to 1200° C. for a time sufficient to form a diffusion alloy of chromium and aluminum on said refractory metal piece,

cooling said box in a protective atmosphere, and

removing said refractory metal piece from said reactive mass.

12. The method according to claim 11 wherein said refractory metal piece is made of a nickel base refractory alloy.

13. The method according to claim 11 wherein said refractory metal piece is made of a cobalt base refractory alloy.

14. The method according to claim 11 wherein said ultra-fine alloy powder further comprises silicon in a proportion by weight in the range of 3 to 10%.

15. The method of claim 1 in which said ultra-fine chromium powder is magnesothermic chromium.

16. The method of claim 1 in which said ultra-fine chromium powder is electrolytic chromium.

17. The method of forming a diffusion alloy of chromium and aluminum on a refractory metal piece made, at least in the superficial part thereof, of at least 50% by weight of a material selected from the group consisting of iron, nickel, cobalt, tungsten, molybdenum and alloys of at least two of said group thereof, which method includes;

preparing a fine magnesium or calcium vapor-treated chromium powder having a mean grain size not substantially greater than twenty microns;

forming an intimate mixture of, first said magnesium or calcium vapor-treated chromium powder, second an aluminum powder in an amount ranging from 5 to 25% by weight of the chromium-aluminum portion of said intimate mixture, third a powdered chemically inert diluting component consisting of an oxide which does not appreciably decompose at temperatures ranging from 750° to 1200° C. and, fourth a halogen containing component of the group consisting of halogens, halides, hypohalogenites and the mixtures of said group thereof;

placing the whole of said mixture in a partly gastight box and placing said box in a heating vessel wherein there is an at least partly hydrogenated protective atmosphere;

heating said vessel and its contents at a temperature ranging from 750° to 1200° C. for a time ranging from a portion of one hour to some twenty hours whereby to form a chromium-aluminum alloy powder;

cooling said box and its contents in a protective non-oxidizing atmosphere;

incorporating said alloy powder in a reactive mass comprising the three following components intimately mixed together, first said alloy powder, second a chemically inert powdered diluting component consisting of an oxide that does not appreciably decompose at a temperature ranging from 750° to 1200° C. and, third a halogen containing compound adapted to be changed into a vapor by heating;

embedding said refractory metal piece in said reactive mass;

placing the whole of said reactive mass and said embedded refractory metal piece in a partly gastight box and placing said box in a heating vessel wherein there is an at least partly hydrogenated atmosphere;

heating said vessel at a temperature ranging from 750° to 1200° C. for a time ranging from a portion of one hour to some twenty hours, and

cooling said box and its contents in a protective non-oxidizing atmosphere.

18. The method of claim 1 in which said chromium powder has a mean grain size not greater than about one micron.

19. The method of claim 1 in which said chromium powder has a mean grain size not greater than about one micron.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,690,934 Dated September 12, 1972

Inventor(s) Philippe Marie Galmiche et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, after line 10, insert -- Claims priority, application France, June 24, 1966, 66,908 --.

Signed and sealed this 15th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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