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DIFFUSION COATING OF METALS

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This invention relates to the diffusion coating of metal articles by dry pack impregnation for the production of an outer metallic layer or coating thereon and, more particularly, to such coating techniques whereby the coating pack is readily regenerated for repeated use notwithstanding the tendency of components in the coating pack to produce an increasing residuum of non-reactive products with each subsequent re-use thereof.

Diffusion coating techniques and procedures of the character to which this invention relates may be illustratively exemplified by those as disclosed in, for example, compending application Serial No. 807,025, filed April 17, 1959, and that of De Guisto and Wachtell, Serial No. 29,150, filed of even date herewith, and the like. As will be understood, such procedures involve embedding a metal article to be coated in a dry impregnating pack comprising a mass of inert mineral filler material, a source of the metal or metals to be coated by diffusion into the surface of the embedded article to be coated in a dry impregnating pack comprising a mass of inert mineral filler material, a source of the metal or metals to be coated by diffusion into the surface of the embedded article, and a source of a volatile or vaporizable halogen substance as a carrier for the coating operation. Upon sealing the pack and heating to a substantial temperature for a period of time, the metal to be coated, apparently through combination with the vaporized halogen, is diffused into the surface of the embedded article to produce in the surface thereof the desired diffusion coating.

Also, as will be understood, a variety of coating metals may be diffusion coated singly or in combination into the surfaces of articles of varying metallic compositions for a variety of purposes, yet all using the dry pack impregnation technique including embedding the article in a mineral filler and utilizing a source of vaporizable halogen material. Thus, metallic chromium may be diffusion coated into the surface of ferrous articles or molybdenum articles or other materials, as may, also, aluminum, silicon, etc.; and iron, alone or in combination with other materials, may be diffusion coated into the surface of various non-ferrous articles by processes generally of the character here designated as dry pack impregnation processes.

Although, in considering such pack diffusion processes, it may be most usual to speak primarily of the chemical reactions involved as between the coating metal in the pack and the halogen component thereof in the diffusion of the coating into the surface of the article being coated, it is also to be understood that a variety of other associated or concomitant or ancillary chemical reactions may also occur during the heating of the pack among the various components therein. For example, there may be a reaction between the coating metal and the halogen for forming a halide, with a further exchange reaction at the surface of the article being coated in which the coating metal is deposited and a halide is formed with the metal of the article. Also, there may be similar reactions as between the coating metal, the halogen, and, for example, the metal of the retort in which the pack is enclosed during the coating cycle.

If more than one material is being coated (as, for example, the use of ferrochromium as a source of chromium which also incidentally includes iron or the simultaneous coating of chromium and aluminum, etc.), there may be a variety of reactions between the metals of the coating and the halogen, as well as reactions between the various

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metals of the coating, producing a variety of resultants which may or may not enter into the actual coating operation. Similarly, if the actual diffusion coating is accompanied by the ultimate production of a halide of one of the metallic components of the article being coated, a further component is developed in or added to the coating pack.

As will be understood from the foregoing, resultant halides or other compounds of the article being coated which are evolved in the pack, as well as other unreactive resultants which may be produced in the pack and do not enter ultimately into the formation of the desired diffusion coating, must all be accommodated or absorbed or eliminated to avoid wastefully contaminating the pack with undesired components and to avoid the formation of absolute equilibrium conditions in order to force to completion the particular reaction or reactions which will be productive of the desired diffusion coating in the surface of the article to be coated.

If it is desired, as frequently may be the case particularly in the day-to-day production coating of a large number of articles, for the same pack to be reused again and again for a number of sequential coating operations, difficulty may be experienced if non-reactive materials resulting from previous coating steps accumulate or build up in the pack. That is, particularly when a large number of small articles are to be coated on a production basis, it may be economically or otherwise desirable to reuse the coating pack many times (with, of course, replenishment of the materials exhausted therefrom) rather than dumping the entire pack after each coating step and making up a wholly new pack for the next batch of articles. In such situations, however, if the various ancillary resultants of the chemical reactions from previous coating steps are allowed to accumulate in the pack during subsequent batches, the difficulty may arise where the efficiency of the pack eventually becomes appreciably diminished, even despite the replenishment of such of the starting materials as are actually incorporated into the coating. Thus, as the quantity or proportion of materials produced by the chemical reactions involved in the coating builds up in the pack, it may become increasingly difficult to drive the particular reaction which is productive of the coating satisfactorily to completion as the concentration of by-products of such reaction not productive of the coating increases in the pack.

As illustrative of such a situation, one particularly emphatic example may be noted in the case where it is desired to produce a diffusion coating containing both chromium and aluminum into the surface of a metal article. Apparently as a part of one or another of the chemical reactions involved in such a diffusion coating, there is produced a substantial proportion of chromium aluminide in the pack, apart from that portion of the original chromium and aluminum that is actually diffused into the desired coating. Aside from the fact that such production of a chromium aluminide which is not a part of the coating is wasteful of two of the active and expensive ingredients of the pack, the continued accumulation or increase in the concentration of chromium aluminide in the pack appreciably may diminish the efficiency thereof for subsequent re-use—either because of occupying space desired for the flow of the diffused materials or because of making it increasingly difficult, on the law of mass action, to force the desired diffusion reactions to completion to produce the diffused coating satisfactorily in the surface of the articles being coated.

According to this invention, however, there is provided, for such diffusion coating operations, procedures and materials for regenerating such coating packs for subsequent and repeated re-use and whereby useless or unreactive resultants of the chemical reactions therein

during one coating operation are broken down in the pack into their respective components useful in providing the coatings of a subsequent coating operation and/or eliminated or regenerated to avoid the undesirable increase or accumulation of the concentration in the pack of non-productive resultant materials formed during each subsequent coating operation, and the invention includes, to this end, the utilization of material such as ammonium fluoride or ammonium bifluoride as at least a part of the halogen component in the pack for packing and breaking down in subsequent coating operations of desired resultants of the chemical reactions occurring in prior coating operations with the same coating pack.

With the foregoing and other objects in view, this invention will now be explained in more detail, and other objects and advantages thereof will be apparent from the following description and the appended claims.

As is now understood, there is a variety of halogen-engendering substances with which satisfactory results may be achieved in diffusion coating processes of the character to which this invention relates. Thus, various halides provide satisfactory uses and, in some instances, elemental iodine is satisfactory or even preferred for some coating packs. As will be understood of course, the natural state of elemental bromine, chlorine, and fluorine, do not adapt these halogens for direct inclusion into a dry pack impregnating process as here. Also, various metallic ions have been proposed for such halide substances, with, perhaps, the ammonium ion being suggested, in many instances, as preferred because, perhaps, of the desirably reducing atmosphere in the sealed pack obtained therefrom during coating, although, in some instances where the material of the coating and/or the metal article being coated are desired to be maintained in a nitrogen-free and hydrogen-free atmosphere during the coating operation, an ammonium salt is not preferred.

With many such coating operations, the choice of a particular halogen or halide substance may not involve a matter of technological criticality, either because for one reason or another the pack is intended for a single use and not for repeated re-use or because the particular coating operation is not productive of an undesirable or wasteful intermediate or other product as noted above or for a variety of other reasons. In such situation, then, ammonium fluoride, for example, might give quite satisfactory results as the halogen material and comparable to those achieved with, for example, the more usual ammonium iodide or iodine or other halides or combinations thereof, except, of course, that the inherent unpleasantness in practice of utilizing ammonium fluoride in such processes, particularly noting the high temperatures at which they are routinely carried out, might suggest that other halides or halogen materials were to be preferred, if only from the standpoint of operating convenience.

In situations, however, such as here where the particular coating operations being carried out include the inherent tendency or capability of producing or engendering during each coating operation a wasteful or unproductive resultant product in the pack which renders it difficult or impossible regenerating the same pack for a subsequent coating operation, satisfactory results have been achieved in accordance with this invention by including as all (or at least a substantial part of) the halogen-engendering component of the pack active halides such as ammonium fluoride or ammonium bifluoride.

For example, as noted above, diffusion coating operations in which both chromium and aluminum are desired to be diffused as constituents of the coating into the surface of a metal article appear to be accompanied by the formation of chromium aluminide in substantial proportions which, on the one hand, use up part of the chromium and aluminum originally added to the pack to be diffused into the desired coating and, on the other hand, remain in the pack without being diffused into

the coating on the article. In such event, it has been found that difficulties arise with the re-use of the same pack for a subsequent coating operation on a subsequent batch of articles to be coated, and even if the expended chromium and aluminum and halide are replenished in the pack.

According to this invention, however, if ammonium fluoride or ammonium bifluoride is included in the pack (at least in the subsequent re-uses thereof) as the source of vaporizable halogen, these compounds, or the decomposition products thereof, appear to attack and break down such undesired or non-productive resultants, as, for example, chromium aluminide and render the components productive or useful for diffusion into the surface of articles being coated in the re-used pack, whereas it has been found, by contrast, that other halides and, even elemental iodine, do not have this reactive or desirable or productive effect during the re-use and regeneration of a used coating pack.

As will be apparent from the foregoing discussion, such breaking down of intermediary or non-productive products or resultants from previous coating operations serves the multiple advantage of eliminating from the pack excessive accumulations of a resultant of chemical reactions therein which might adversely influence either the efficiency of the pack or the ease with which the desired reaction producing the coating can be driven to completion, while also utilizing for enhanced efficiency a maximum proportion of the chromium or aluminum metals added to the pack for producing the coating instead of wastefully producing useless chromium aluminide. Thus, such a coating pack may be regenerated for repeated reuse in accordance with this invention, and also produces an enhanced overall yield of the added coating materials, it being understood, of course, that some proportion of the coating metals, as well as the halide, are to be replenished after each repeated use of the pack.

As purely illustrative of one embodiment of a process in accordance with this invention, a plurality of inlet stator vanes for a gas turbine engine were cast of an alloy consisting of about 55% cobalt, 24.5% chromium, 10.5% nickel, 715% tungsten, and 0.5% carbon. After casting, these vanes were embedded in a coating pack containing approximately 59.75% alumina as the inert filler material, 30% chromium metal, 8% aluminum metal, and 2% silicon, all as the materials to be diffused into the vanes as a silicon-chromium-aluminum coating thereon. In the pack was also incorporated 0.25% ammonium bifluoride, and the coating operation carried out in the usual manner as by sealing the pack into an iron retort and heating the sealed retort for from 4 to 20 hours at temperature of about 1800° F. to 2100° F. to produce the desired coating.

After cooling, the retort was opened and the coated vanes removed for use. A subsequent batch of the same vanes are then added to the pack, along with a replenishing quantity of chromium and aluminum and silicon as may be needed (depending upon, of course, the thickness of the coating desired on the vanes and the relative proportion of surface to be coated to the total quantity of pack constituents, etc.) and a subsequent operation carried out with satisfactory results in approximately the same length of time at the same temperatures and with approximately the same recovery or yield of materials being coated into the surface of the metal articles. It has also been found that, if ammonium iodide were utilized, instead of the ammonium bifluoride, re-use of the pack would be either impossible or would require a substantially extended period of heat treatment with appreciably less yield of materials, and, as further repeated re-uses were attempted, despite the replenishing of the pack with fresh quantities of the materials to form the coating and halogen energizer, the pack would rapidly come to the

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point where virtually no diffusion coating was being obtained.

As further illustrative examples of procedures of a coating operation embodying and for practicing this invention, one may note the following compositions of various coating packs to which are applicable the teachings of this invention (the parts being by weight):

Example I

70 parts alumina 10
22 parts chromium
8 parts aluminum
1/4 part ammonium bifluoride

Example II

70 parts alumina 15
22 parts chromium
8 parts aluminum
1/3 part ammonium fluoride 20

Example III

65 parts alumina
33 parts chromium
2 parts aluminum 25
1/4 part ammonium bifluoride

Example IV

65 parts alumina
33 parts chromium
2 parts aluminum
1/3 part ammonium fluoride

Example V

65 parts alumina
23 parts chromium
12 parts aluminum
1/4 part ammonium bifluoride

Example VI

65 parts alumina
23 parts chromium
12 parts aluminum
1/3 part ammonium fluoride 45

Example VII

60 parts alumina
30 parts chromium
8 parts aluminum
2 parts silicon
1/4 part ammonium bifluoride 50

Example VIII

60 parts alumina
30 parts chromium
8 parts aluminum
2 parts silicon
1/3 part ammonium fluoride 55

Example IX

60 parts alumina
31 parts chromium
8 parts aluminum
1 part silicon
1/4 part ammonium bifluoride

Example X

65 parts alumina
31 parts chromium
8 parts aluminum
1 part silicon
1/3 part ammonium fluoride

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Example XII

65 parts alumina
30 parts chromium
3 parts silicon
2 parts aluminum
1/4 part ammonium bifluoride

Example XIII

65 parts alumina
30 parts chromium
3 parts silicon
2 parts aluminum
1/3 part ammonium fluoride

Example XIV

70 parts alumina
20 parts chromium
5 parts aluminum
5 parts silicon
1/2 part ammonium bifluoride

Example XV

70 parts alumina
20 parts chromium
5 parts aluminum
5 parts silicon
1/3 part ammonium fluoride

As further illustrative of coating packs useful in connection with this invention and in which the cation of the fluoride or bifluoride regenerator is different from ammonium (as may be desired in certain coating applications, although the ammonium cation is useful as generating itself a reducing atmosphere), the following may be noted:

Example XVI

70 parts alumina
22 parts chromium
8 parts aluminum
.1 part ammonium bifluoride
.3 part chromous fluoride

Example XVII

70 parts alumina
22 parts chromium
8 parts aluminum
.15 part ammonium fluoride
.3 part chromous fluoride

Example XVIII

60 parts alumina
30 parts chromium
8 parts aluminum
2 parts silicon
.1 part ammonium bifluoride
.3 part chromous fluoride

Example XIX

60 parts alumina
30 parts chromium
8 parts aluminum
2 parts silicon
.15 part ammonium fluoride
.3 part chromous fluoride

65 In accordance with the foregoing, then, a variety of useable coating packs are achieved with which enhanced results may be experienced utilizing as the halogen component thereof a fluoride, instead of another halide. Such enhanced results may particularly be notable with regard to the reuse of diffusion coating packs in which, during a first heating or diffusion coating operation components originally in the pack may tend to form in the pack certain intermetallic associations such as chromium aluminide. That is, particularly in cases where the pack 75 contains separate or other sources of chromium and

aluminum for diffusion coating, one of the resultants of heating such a pack, even with articles to be coated therein, may be the formation or association of chromium and aluminum into an intermetallic substance such as chromium aluminide which is resistant to subsequent attack or thermal or chemical decomposition by halides other than the fluoride so that re-use of such a pack in a subsequent operation may require a complete replenishment of sources of chromium and aluminum, although these materials remain in the pack from a previous coating operation in the intermetallic combined form but substantially inert to energization or diffusion by the halide carrier present if it be other than the fluoride. The utilization of a fluoride as the halide carrier or energizer, however, appears to attack or break down or render useful for diffusion coating intermetallic substances such as chromium aluminide formed in the pack in a previous coating operation, thereby enhancing the efficiency of utilization of the treating materials and re-use of any particular coating pack.

It is, of course, to be understood that the foregoing description is illustrative only and that numerous changes may be made in the conditions, proportions, and ingredients specifically disclosed without departing from the spirit of the invention as defined in the appended claims.

What is claimed is:

1. In a pack impregnation diffusion coating of the character described for producing an outer layer of metallic constituents diffused into the surface of a metal article, the steps which comprise embedding said metal article in a diffusion coating pack including a source of chromium and aluminum as the metallic materials to be diffusion coated into the surface thereof and a source of vaporizable halogen for diffusion of said materials into said metal article, heating said pack with said materials and said article therein effecting vaporizing of said halogen and diffusion of said metallic materials into the surface of said article, also producing in said heating and diffusion coating step resultant components in said pack including chromium aluminide which are not diffusion coated into the surface of said article, removing said thus coated article from said pack, embedding a subsequent article to be coated in the same said pack for re-use thereof and a subsequent diffusion coating operation, including in said pack at least in said subsequent coating operation a fluoride as at least a part of said vaporizable halogen component, heating said article embedded in said pack in said subsequent coating operation for diffusion coating of said metallic materials into the surface thereof, and effecting by thermal reaction with said fluoride breakdown of said resultant chromium aluminide components formed in said preceding coating step for a diffusion coating thereof into said article in said subsequent coating step in said pack.

2. In a method for the dry pack impregnation diffusion coating of metallic substances including chromium and aluminum into the surface of a metal article embedded in said pack and which pack includes a portion of said metallic materials as chromium aluminides and in a form which is stable and not susceptible to diffusion coating into the surface of said article, the steps which comprise introducing into said pack a vaporizable fluoride, heating said pack with said article embedded therein and said stable aluminide form of said metallic materials in the presence of said vaporizable fluoride to a temperature substantially above the vaporization temperature of said fluoride, effecting conversion and breakdown of said stable form of said metallic materials by reaction with said fluoride and diffusion coating said chromium and aluminum metallic materials individually into the surface of said metal article for producing said diffusion coating.

3. In a method for the re-use and regeneration of a diffusion coating pack for a subsequent coating of

metallic materials including chromium and aluminum into the surface of a metal article after a previous metal article has been diffusion coated in same pack in a previous coating step which produced in the pack residual components including said metallic materials in a stable chromium aluminide form not susceptible to direct diffusion into the surface of said metal article in said subsequent coating step, the steps which comprise including in said pack a vaporizable fluoride for reacting with said residual stable chromium aluminide metallic materials to convert them into a form susceptible for diffusion coating into said article in said subsequent coating step, heating said pack in said subsequent coating step with said article and said residual stable metallic materials and said vaporizable fluoride therein to a temperature substantially above the vaporization temperature of said vaporizable fluoride effecting conversion of said residual metallic materials with said fluoride to a form susceptible to diffusion coating into the surface of said metal article, and maintaining said heating for transfer and diffusion coating of said reacted metallic materials into the surface of said metal article for forming said diffusion coating.

4. In a method for the dry pack diffusion coating of a combination of substances including chromium and aluminum into the surface of a metal article embedded in a diffusion coating pack along with a vaporizable halogen, the steps which comprise heating said pack for the diffusion coating of said materials including said chromium and aluminum into the surface of said metal article in a first coating operation, effecting during said first coating operation the production of a stable component in said pack including chromium and aluminum in a form not susceptible to direct diffusion coating into the surface of said article, after said first coating operation utilizing said same pack for the diffusion coating of a subsequent metal article in a second coating operation, including in said pack at least during said second coating operation and as at least a portion of said vaporizable halogen therein a vaporizable fluoride, effecting reaction during said second coating operation of said fluoride with said stable form of said metallic materials for breaking down said stable form of said metallic materials into a form susceptible for diffusion coating into said article in said subsequent coating operation, and diffusion coating said metallic materials from said first coating operation into the surface of said metal article during said second coating operation for forming said diffusion coating in the surface of said article.

5. In a method for regenerating for re-use a dry diffusion coating pack which includes a residuum of stable and uncoatable metallic components including chromium aluminides produced during a preceding diffusion coating step in order to produce in a metal article to be coated with said pack in a subsequent coating step a diffusion coating of chromium and aluminum, the steps which comprise including in said pack at least during said regenerating and subsequent coating step a vaporizable fluoride, heating said pack with said article to be treated and said fluoride therein to a temperature sufficient for said fluoride to react with said residuum of chromium aluminides effecting conversion and reaction thereof into a coatable form, and maintaining said heating for coating of said reacted chromium and aluminum into the surface of said article to be coated in said subsequent coating step in the absence of formation of further stable residual components in said pack preventive of the subsequent regeneration thereof for further subsequent coating steps.

6. In a method for the dry pack impregnation diffusion coating of metallic chromium and aluminum into the surface of a metal article embedded in said pack with re-use of said pack for diffusion coating of subsequent metal articles, the steps which comprise forming said pack including a source of metallic chromium and alu-

minum in proportions which form a stable chromium aluminide upon heating said pack, embedding said metal article to be coated in said pack, heating said pack effecting said diffusion coating of a part only of said metallic chromium and aluminum into the surface of said metal article and causing combination of other portions of said chromium and aluminum to form said stable chromium aluminide, removing said thus coated metal article from said pack, including in said pack a vaporizable fluoride, embedding in said pack a subsequent metal article for a subsequent coating step, heating said pack for said subsequent coating step to a temperature above the vaporization temperature of said fluoride effecting decomposition of said stable chromium aluminide formed in said first step by said vaporized fluoride during said subsequent heating, and diffusing chromium and aluminum from said decomposed chromium aluminide into the surface of said subsequent metal article in said subsequent coating step.

7. In a method for the dry pack diffusion coating of chromium and aluminum into the surface of a metal article embedded in a powdered diffusion coating pack including chromium and aluminum preponderantly in stable intermetallic chromium aluminide form substantially resistant to diffusion coating, the steps which comprise introducing a solid fluoride into said coating pack, embedding a metal article to be coated in said pack, and heating said pack to a temperature substantially above the vaporization temperature of said fluoride, effecting breakdown of said chromium aluminide by reaction with said fluoride and diffusion coating of said chromium and aluminum individually to the surface of said metal article.

8. A re-useable and regeneratable dry coating pack for the impregnation diffusion coating of metallic components including chromium and aluminum into the surface of a metal article to be coated, comprising in combination a substantial portion of mineral filler, a por-

tion of stabilized and essentially non-coatable metallic materials including chromium aluminides as a residuum in said pack resulting from previous coating operations in which said stable aluminide form of said chromium and aluminum components to be coated was produced as a by-product of the previous coating operations, and a vaporizable fluoride for regenerating said pack upon re-use and for reaction with said stable aluminide form of said chromium and aluminum components to render them into a coatable state for diffusion coating in said repeated and re-used pack into the surface of a metal article embedded in said pack for coating during said re-use and regeneration thereof.

9. A regeneratable dry coating pack for the diffusion coating of chromium and aluminum into the surface of a metal article to be embedded in said pack during a diffusion coating step, comprising a substantial portion of inert refractory filler, a source of chromium and aluminum for said diffusion coating but with said chromium and aluminum being substantially entirely combined into intermetallic chromium aluminide in a stable form resistant to thermal decomposition for said diffusion coating, and a vaporizable fluoride material for vaporizing upon heat of said pack during said diffusion coating and for decomposing said stable chromium aluminide form to provide said chromium and said aluminum individually into diffusible and coatable form for diffusing into said metal article.

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