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# DIFFUSION COATING OF METALS

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## ABSTRACT OF THE DISCLOSURE

In pack impregnation or cementation processes for the diffusion coating of one or more metals into the surface of metal articles, improved techniques and compositions are provided for the diffusion coating of metals such as aluminum and antimony into the surface of a variety of ferrous and other metal articles embedded in a powdered coating pack at coating temperatures considerably lower (by as much as 200° F.) than those temperatures required by conventional techniques to provide effective diffusion coating of the same materials. This is accomplished by providing in the coating pack an accelerating component (such as either relatively volatile metals as cadmium, lead, zinc, etc., or certain long chain organic compounds) which do not ultimately form a substantial or significant part of the diffusion coating, but do act in the coating pack to accelerate the diffusion of the coating metals into the articles being coated at lower temperatures to achieve increased coating deposition at a given temperature and/or satisfactory coating deposition at temperatures lower than otherwise obtainable, and permitting satisfactory coatings at temperatures below those at which some undesired crystallographic or metallographic or physical property change would occur in the metal articles being coated.

This invention relates to the pack cementation diffusion coating of metals into the surface of metal articles embedded and heated in a diffusion coating pack and, more particularly, to techniques and compositions whereby an accelerator component for the diffusion coating is included in the pack to accelerate or increase the diffusion of the coating metal from the pack into the surface of the articles being coated, permitting either a greater diffusion at a given temperature and/or satisfactory diffusion coatings at coating temperatures lower than those required with conventional diffusion coating processes.

The types of diffusion coating techniques to which this invention generally relates will be recognized and understood as those diffusion coating processes in which the metal articles to be coated are embedded in a powder pack including, generally, the coating metal (in this case, such metals as aluminum or antimony), usually an inert filler (such as powdered alumina), and an energizer component (such as a halogen or readily vaporizable halide) for aiding the transfer of the coating metal from the powdered pack to the surface of the articles to be coated, and then heating the articles embedded in such pack in a closed retort (usually in the absence of oxygen) to relatively high temperatures for sufficient time to produce the diffusion of the coating metal into the surface of the articles to the desired depth. Such processes are well known for enhancing the oxidation resistance (particularly for high temperature use), erosion resistance, corrosion resistance, etc., of the base article for a variety of purposes and uses, and, as well understood, such pack cementation diffusion coating techniques may require that the coating step be prolonged for many hours, or even more than a day, at relatively high temperatures (e.g., 1800°–2000° F. and usually higher than 1200° F.), depending upon the particular metal composition of the coating and the thickness of coating desired and other characteristics.

Nevertheless, there is a variety of metals and metal alloys the physical or mechanical properties of which are altered or adversely affected when they are heated above, for example, 1000° F. for any reason, yet where the ultimate properties or useful life of articles made from such metals or metal alloys would be significantly enhanced if the articles could be given a diffusion coating for resisting corrosion or oxidation or erosion, etc. For example, the tempering temperature for some conventional hardenable stainless steel alloys is approximately 1000° F. If it is attempted to apply any sort of diffusion coating into the surface of an article made from such materials, obviously, the crystallographic structure or mechanical properties of the article will be altered during the coating process if the latter requires heating to a temperature 1000° F. or above, and such alteration of the base metal article may render it mechanically unsuited to the desired use, whether or not a surface diffusion coating is successfully applied thereto.

For example, certain components of the compressor portions of jet aircraft engines are made of certain high strength steels because they are subjected to tremendous mechanical stresses from centrifugal force, thermal shock, and vibration, although the actual operating temperatures rarely exceed about 900° F., so that there is little need to provide either extremely high temperature materials or high temperature oxidation resistant coatings, as is the case, by contrast, with the turbine components of the jet engine subjected to the much higher temperature of the impinging combustion gases. Nevertheless, considering low flying aircraft operating or based near the seashore in highly saline atmosphere which may also include substantial amounts of sand or coral dust (e.g., helicopters operating near sea coasts), it may be highly desirable to provide compressor portions of such aircraft engines with a surface diffusion coating which is galvanically sacrificial and resistant to dust erosion and/or saline corrosion, especially localized or pitting corrosion, even when such parts do not require extremely high temperature oxidation resistant coatings as is usually required for the high temperature turbine portions of such jet engines.

Yet, the important aspect of such compressor parts is the mechanical strength thereof to resist mechanical and thermal shock forces, and the failure of such parts (particularly in aircraft with but a single engine) would be catastrophic. Thus, if it is attempted to provide a corrosion or erosion resistant coating on such parts by conventional coating techniques, it may be found that the necessary thermal or other coating conditions for achieving the coating in the first place have a degrading effect on the essential mechanical properties of the parts—e.g., in the manner that the mechanical or metallurgical characteristics of certain steel alloys would be degraded by a post-fabrication treatment involving heating above 1000° F., but where applying a conventional aluminum coating to such parts would require coating temperatures in the range of 1000°–1500° F. in order to achieve a satisfactory aluminized coating.

Thus, for a variety of well understood reasons, coating materials such as aluminum or antimony are difficult, if not impossible, to diffusion-coat into the surfaces of various ferrous metal alloy articles to achieve a satisfactory coating on the completely fabricated and finished article at coating temperatures less than those which would inherently alter or degrade the mechanical or metallurgical properties of the article being coated. Furthermore, even with the diffusion coating of such metals as aluminum or antimony into the surface of other metal articles formed or fabricated of alloys readily able to withstand coating temperatures in the vicinity of 1500° F., adequate coating depths may require extended coating times (up to 30 hours or more) and longer than may be economically desirable from the standpoint of commercial practice.

In accordance with this invention, by contrast, there are provided techniques and compositions for accomplishing the satisfactory coating diffusion of metals such as aluminum and antimony into the surfaces of metal articles having compositions which comprise iron, chromium, titanium, nickel, cobalt, etc., by pack cementation processing at lower temperatures than are conventionally utilized and/or at higher rates of deposition at a given temperature compared with conventional pack cementation processes, by including in the powdered pack an accelerator component (either metallic such as cadmium, lead, and/or zinc, or organic such as long chain organic hydroxy or carboxy compounds), which accelerator component has the effect in the pack of increasing the rate of deposition of the coating material into the surface of the article being coated without a substantial or significant proportion of the accelerator component itself being diffused into the article being coated along with the coating metal. As a further feature of the invention, it is thus possible, not only to increase the rate of deposition of the coating metals onto the article being coated (thus in many instances decreasing the time necessary to achieve a desired coating of adequate thickness), but also to achieve satisfactory coating results at temperatures lower than conventionally required, thus permitting the coating of metal articles which undergo a thermally induced metallographic or physical change at temperatures below conventional coating temperatures.

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

Merely as illustrative of techniques and conditions embodying and for practicing this invention, one may consider the diffusion coating of aluminum by pack cementation processes into the surface of various metal articles of differing compositions, and, as is well understood, one may note that, according to conventional techniques, such aluminum diffusion coatings are conventionally produced at coating temperatures generally above 1500° F. and, in some cases and particularly with the so-called "super alloys," as high as 1800° or 2000° F. or more. Thus, attempts to aluminize steel alloys such as those designated as AMS 5616 in the Aerospace Material Specifications of the Society of Automotive Engineers (which are generally characterized as including about 13% chromium, 2% nickel, and 3% tungsten) with a conventional alumium diffusion coating pack comprising by weight, 20% aluminum powder, 0.5% ammonium iodide, 0.25% urea, and balance alumina filter, at temperatures below 1000° F. resulted in the deposition of a thin and quite irregular coating even after extending the coating thermal cycle to as long as 24 hours, which coating was completely unsatisfactory. Indeed, as will be understood, even with such a long coating cycle, satisfactory results would not be expected at coating temperatures of below 1050° F.

Nevertheless, the addition of about 1% powdered cadmium metal to the coating pack, in accordance herewith, produced satisfactory results at coating temperatures of about 900° F. and, actually, at temperatures as low as about 850° F. without excessively long coating times. A satisfactory aluminum coating, of about 1 mil thickness, was deposited at 900° F. within a 24 hour cycle, with the characteristics of the finished coating being satisfactory, with a smooth surface finish, and comparable to coatings produced from pure aluminum packs at temperatures above 1100° F.—i.e., the coating was free of micro cracks and afforded good corrosion and erosion resistance in a saline marine environment. Most importantly, the mechanical properties of the base steel alloy were not impaired or significantly altered as would be the case with coating temperatures at or above 1000° F.

Some acceleration effect of the cadmium addition was noted when only 0.125/ cadmium was added to the pack, and no significant increase in the degree of acceleration of aluminum deposition was noted as a result of increasing the cadmium addition above 0.25%. With cadmium present in the pack at concentrations approaching about 5%, there was noted a tendency for the cadmium to condense on the surface of the aluminized layer, and, for the foregoing reasons, a cadmium addition of about 1% appears to be preferred in accordance herewith from a practical standpoint and, especially, in those commercial applications where the coating pack ingredients will be reused for a number of coating operations subject only to replenishment of those components which are expended in the coating cycle (e.g., aluminum coating metal, halogen energizer, etc.).

The mechanism responsible for the acceleration effect in accordance herewith of such metals as cadmium and those others noted more specifically below may not yet be completely understood, but it may be useful to hypothesize that the enhanced results are somehow associated with the high vapor pressure exhibited by cadmium at the coating temperature in the coating pack environment. A chemical type of acceleration with actual chemical combinations of the accelerating component with the coating materials does not appear to be involved because, for example, cadmium metal is relatively insoluble in both iron and aluminum. Little or no cadmium was detected by electron microprobe analyses of the resulting coating, which indicated a surface composition of approximately 60% aluminum and the balance mainly iron—i.e., a composition corresponding generally to the intermetallic compound $FeAl_3$.

The insolubility of cadmium in iron also suggests why cadmium is not deposited as a part of the coating. Although discussed in more detail below, the foregoing is somewhat further confirmed by attempts to utilize zinc and magnesium (both of which have relatively high vapor pressures in the coating environment) as accelerating components for aluminum diffusion coatings. Although zinc also shows a marked tendency to accelerate the aluminum deposition in accordance herewith, the solubility of zinc in iron permitted a significant co-deposition of zinc with aluminum in the substrate. Indeed, a preferred accelerator combination, particularly for ferrous base metals may include an addition of 1% of each cadmium and zinc powder to the coating pack. Despite the high vapor pressure achieved with magnesium, magnesium additions appear greatly to inhibit desired aluminum deposition on such ferrous substrates.

In addition to generally ferrous substrates, it has also been found in accordance herewith that metals such as cadmium provide the desired accelerating effect in the aluminizing of metal articles having high chromium content. Thus, using a conventional cementation pack containing about 20% aluminum powder, 0.5% ammonium iodide in a preponderant amount of alumina filler (with or without 0.25% urea), a substantial and satisfactory amount of aluminum was deposited in accordance herewithin into a chromium substrate at temperatures as low as only 900° F. upon the addition of 0.5% to 5% cadmium metal to the coating pack, whereas, with the same pack but in the absence of the cadmium as an accelerating component, a negligible amount of aluminum deposition was noted. As illustrative, a coating of 1–2 mil thick was readily and satisfactorily deposited in a 30 hour coating cycle at 900° F. utilizing a cadmium accelerator in accordance herewith, whereas a coating of only less than 0.1 mil thick was deposited on the same chromium substrate under the same coating conditions but without the addition of the cadmium accelerator.

It may be noted that the practical reasons for desiring lower coating temperatures with high chromium substrates may be somewhat different than those noted above regarding steels or ferrous or titanium alloys where the primary consideration is high mechanical strength. Thus, with high chromium alloys and/or other high temperature "superalloys" having high nickel or cobalt concentrations along with substantial and important concentrations of chromium, a substantial depletion of chromium from the surface of the article (by the diffusion or dissolving of the chromium back into the interior of the article and away from the surface) is noted when such articles are aluminized with conventional high temperature aluminizing techniques, so that the utilization of an accelerator in accordance herewith maintains the desired substantial concentration of chromium at the surface of the article, along with nickel or cobalt or iron, as the case may be, for combination with the aluminum being diffused into the surface. That is, as is well understood, especially with high temperature alloys and to achieve enhanced high temperature oxidation resistance with aluminizing techniques, it is apparently the provision at the surface of the desired combination of chromium, iron, nickel, and/or cobalt aluminides which achieves the results desired, and such results may be impaired if such high coating temperatures are required that a substantial portion of the chromium is driven back into the article and away from the surface thereof.

In addition to cadmium and zinc as appropriate accelerator metals in accordance herewith, satisfactory results have also been achieved utilizing lead as an appropriate accelerating addition to the coating pack. For example, additions of between 0.25% and 5% by weight of lead powder to aluminizing packs as noted above have produced satisfactory results in the deposition at about 900° F. of aluminized coatings into the surfaces of articles made from the above noted AMS 5616 steel, AMS 6304 steels (generally characterized as including 1% Cr, 0.55% Mo, 0.3% V, and with carbon contents up to around 0.5%) and 17–4 PH stainless steels (characterized as being precipitation hardenable steels containing about 17% Cr, 4% Ni, 3% Cu, and smaller amounts of Co, Mn, and Si), where attempts to produce satisfactory coatings at comparable temperature and time cycles may fail without the accelerating addition of lead powder to the coating pack.

Although it has been found that the degree of acceleration provided by lead is somewhat less than that provided by cadmium in accordance herewith, the former is considerably less toxic than the latter (it being remembered that the accelerator component is vaporized at the coating temperatures), and lead, therefore, may be preferred from a practical standpoint for large scale production. As will be understood, lead may also be definitely preferred to cadmium for certain applications where cadmium is soluble in the substrate (e.g., nickel substrates) being coated, just as cadmium may be preferred to zinc for use with ferrous substrates in which zinc is relatively soluble.

The effect or degree of acceleration in accordance herewith does not appear to vary appreciably with the selection of the particular halogen or vaporizable halide used as the energizer in the coating pack. That is, cadmium accelerates the aluminizing of steels at 900° F. to a substantial and satisfactory extent in accordance herewith whether the energizer used be an iodide, bromide, chloride, or fluoride. The thickest coatings are achieved with the iodide, but this is not believed to be a function of the accelerator addition to the pack. Similarly, the accelerators in accordance herewith achieve substantially the same degree of acceleration of coating deposition with metal articles which have been previously aluminized according to this or other techniques as are achieved with uncoated or virgin articles, thus suggesting that the accelerating effect is not a surface-related phenomenon.

Similarly, the addition of cadmium iodide (instead of metallic cadmium) to the pack also produces satisfactory accelerating results in accordance herewith in the aluminizing of various substrates at 900° F., and, after the coating cycle is completed, there was found evidence of free cadmium in the coating pack. Thus, the accelerated amount of aluminum deposited on nickel and/or AMS 6304 steel at 900° F. in a pack, such as above, with a 1% cadmium metal addition was almost identical to the amount deposited in a similar pack containing as an accelerating addition 3% cadmium iodide (equivalent to 1% metallic cadmium). Apparently, this may be considered as indicating that the iodine liberated by decomposition of the cadmium iodide functions in somewhat the same manner as the ammonium iodide energizer in a conventional pack and then reacts with the aluminum to form aluminum tri-iodide or a complex of that iodide with cadmium iodide in the conventionally understood mechanics of aluminum transfer to, and decomposition at, the surface of the article being coated caused by the presence of a halide energizer in the pack. Nevertheless, the best results were achieved in accordance herewith by adding fresh accelerator to the pack before a subsequent re-use thereof rather than relying on decomposition during the coating cycle of previously formed cadmium iodide into accelerating metallic cadmium.

Cadmium does not appear notably to enhance the deposition of chromium or titanium coating metals on steel articles below 1000° F., but the reason appears to be the low solubility of chromium or titanium in iron at such relatively low temperatures. Acceleration of the coating of such materials at higher temperatures, however, is also to be comprehended within this disclosure. Both cadmium and lead, when either was present as a 1% addition in a pack comprising 20% antimony, 0.5% ammonium iodide, and balance alumina, increased the rate of antimony deposition in a variety of substrates, with a particularly high degree of acceleration when using steels, such as AMS 6304, and cobalt substrates and, to a smaller degree, nickel substrates. The foregoing observations further confirm the hypothesis that the accelerating results in accordance herewith are related in large manner to the effect of the accelerator materials in increasing the kinetics of decomposition of the halide of the coating material formed in the pack for the transfer of the coating metal onto the surface of the article being coated.

Whereas cadmium accelerates the aluminum deposition on chromium, chromium alloys, and previously chromized superalloys, it appears to have little effect on the rate of aluminum depositions on high nickel or high cobalt superalloys containing substantial amount of chromium, in aluminizing procedures in which the pack is especially formulated to inhibit aluminum deposition at low coating temperatures (such as, for example, the techniques disclosed in Pat. No. 3,257,230). Even after a 20-hour treatment at 1900° F. of superalloy articles (such as W152) in a pack containing both chromium and aluminum as set forth in that patent, the weight gain and finish in packs with and without a cadmium accelerator addition were substantially identical, but this result is believed to be explained primarily by the solid state diffusion rate controlling mechanism of such controlling techniques as being more determinative of final coating results than increasing the aluminum supply to the article surface.

Both cadmium and lead produce satisfactory results as accelerating additives in accordance herewith in the aluminizing of the metal articles formed of titanium and titanium alloys (such as those also containing about 6% aluminum and 4% vanadium). Thus, with treatment at 1000° F. in a pack comprising 20% aluminum, 0.5% ammonium iodide, and the balance alumina, a 1% cadmium accelerator addition doubled the amount of aluminum deposition on titanium during a 12-hour cycle, while an addition of 1% lead increased the deposition by about 1.5 times, and microprobe analyses indicated that neither lead nor cadmium was dissolved or included in the coating or the metal article being coated.

Microprobe analyses of the various coatings produced in accordance herewith have indicated that aluminum coatings produced at 900° F. and 1000° F. from packs in which the accelerating addition was cadmium, were substantially free of cadmium when the substrate was predominantly iron, cobalt, or chromium, whereas some cadmium was found as a co-deposit with aluminum on nickel and nickel alloy articles. As noted above, zinc performs a similar accelerating function on the various substrates noted, although there was found to be some solubility in iron-base articles (perhaps about 5–10%) at the substrate-coating interface. For example, analyses of 1 mil coatings produced on AMS 6304 steel from a pack comprising 20% aluminum, 1% each cadmium and zinc, 0.5% ammonium iodide, and 0.25% urea, with the balance being tabular alumina, by heating at 900° F. for 30 hours showed about 5–10% zinc and about 60–65% aluminum at the substrate-coating interface, the balance being iron.

Lead functions satisfactorily as an accelerating addition in accordance herewith in aluminizing treatments at 900° F. with any of the substrate materials iron, nickel, or cobalt. Although, as noted, lead is a less active or effective accelerator than cadmium with certain materials, the addition of 1% lead to a conventional coating pack as noted above more than trebled the aluminum deposition (for the same temperature and time) with iron, nickel, and cobalt substrates as compared with aluminizing from the same pack without an accelerator addition in accordance herewith. Utilizing tin as the accelerating additive to similar aluminizing packs produces a degree of acceleration substantially like that produced by lead at 900° F. Attempts to use 1% chromium or nickel as accelerator additions in accordance herewith in the aluminizing of iron, nickel, or cobalt substrates at 900° F. produced no appreciably enhanced results at such low temperatures, although cadmium satisfactorily accelerated the degree of aluminum deposition from a pack containing 20% aluminum, 2% chromium, 0.5% ammonium iodide, and the balance alumina.

Both cadmium and lead, as will be understood, have relatively high vapor pressures at 900° F., and the iodides thereof have similar thermodynamic stabilities at this temperature and also high vapor pressures. These factors are believed to be of significance in attempting to explain the mechanics of the accelerating results in accordance herewith. It may be noted, for example, that zinc oxide will reduce aluminum tri-iodide to zinc iodide and alumina at relatively high temperatures (perhaps 230° C.) after prolonged reaction. Similarly, cadmium oxide will reduce aluminum tri-iodide to cadmium di-iodide and alumina under substantially the same conditions. This suggests that the acceleration in accordance herewith occurs by an increase in the reduction of the aluminum tri-iodide (formed in the pack by reaction of the aluminum powder and iodide energizer) with cadmium and/or zinc—thus having the accelerator additives effecting a marked increase in the kinetics of the aluminum tri-iodide reduction necessary for satisfactory deposition for diffusion of aluminum.

X-ray analysis, for example, indicates that the intermetallic compound $FeAl_3$ is formed in the surface coating on the ferrous article being coated at 900° F. with cadmium acceleration in accordance herewith, which compound can be converted to $Fe_2Al_5$ by further diffusion treatment at higher temperatures of 1100° F. and above. Without an accelerating addition in accordance herewith, attempts to produce coatings on steel at lower temperatures and comprising $FeAl_3$ have generally failed, with principally the compound $Fe_2Al_5$ being formed and then only at higher coating temperatures, perhaps indicating that one effect of the accelerating technique in accordance herewith is to provide for more rapid deposition at lower temperatures where solid state diffusion of the coating material into the article being coated is relatively slow.

Although the advantage of working at lower coating temperature has been emphasized above as a principal advantage of the results obtained by utilizing accelerator materials in accordance herewith, it may also be noted that such accelerating techniques also achieve the result of producing observable deposition of coating material in the various substrates in less time and/or more quickly after a start-up of the heating cycle. Thus, for example, cadmium and lead accelerated the aluminizing of iron, cobalt, and nickel in accordance herewith at 900° F. and 1000° F., but were not able to produce an observable deposition of aluminum at 800° F. even during a 30-hour treatment. The rate of aluminum deposition on iron, nickel, and cobalt substrates at 900° F. and at 1000° F. decreased in the order of cadmium, lead, and non-accelerated packs. After 10 hours of processing, the amount of coating deposited in the lead-accelerated pack was approximately one-third that deposited from the cadmium-accelerated pack, and that deposited by the pack without either accelerating additive was only approximately one-fifth of that of the cadmium-accelerated pack. Similarly, the rate of coating deposition in both accelerated and non-accelerated packs decreased with time at both 900° F. and 1000° F.

Nevertheless, an observable amount of aluminum was deposited as a coating from the cadmium-accelerated pack (treating AMS 6304) during the first hour of processing at 900° F., whereas up to 5 hours' processing time was required for appreciable deposition of aluminum from the lead-accelerated pack and between 5 and 10 hours before appreciable coating was noted from the non-accelerated pack. This confirms the suggestion noted above that at least one effect of the accelerating additive is to increase the rate at which aluminum halide decomposition is achieved for transfer of the aluminum into the surface of the article being coated. Also confirming the foregoing is the fact that negligible deposition of aluminum into the steel article was noted even when the pack materials had been reacted for 30 hours at 1000° F. prior to introducing the metal article into the pack. The addition of a cadmium accelerator to the same pre-reacted pack, however, produced observable aluminum coating deposition at 900° F. within the first hour.

Similarly, with treating temperatures at 1000° F., the lengths of treatment times required for a given deposition of aluminum into the steel article also decreased in the order of cadmium, lead, and non-accelerated, thus indicating both a great deposition for a given time and temperature with the accelerated additions and/or a shorter treatment time required for a given aluminum deposit. Considering the latter, specimens of AMS 6304 coated at 1000° F. for 20 hours indicated a final coating thickness of 2.1 mils with a cadmium-accelerated pack, 1.6 mils with a lead-accelerated pack, and only 0.9 mil with a non-accelerated pack, the packs all being the same and as noted above, and the accelerating additions of lead and cadmium being each 1% by weight of the pack.

Although, as noted above, the advantage of extremely low coating temperatures may not be as important with some of the high nickel and high cobalt superalloys as with steels which undergo a variation in mechanical properties, consideration of the results achieved in attempts to produce aluminum coatings on a variety of nickel and cobalt superalloys at low temperatures with accelerated pack additions in accordance herewith may be helpful in considering all aspects of the teachings hereof. Thus, considering as merely illustrative such well known superalloys as B1900, IN100, INCO713, HS21, SM302, and W152, little or no aluminum coating deposition was noted at 900° F. during a 24-hour cycle using aluminizing packs as indicated above accelerated with either cadmium or lead, although the nickel-base superalloys had more of a tendency to be coated than the cobalt-base materials.

At 1000° F., however, a non-accelerated aluminizing pack produced very thin coatings on the nickel-base alloys, whereas accelerating additions of tin, cadmium, and, to a larger degree, lead, showed a considerable deposition of aluminum on both the nickel and cobalt alloys.

In all instances, the coating thicknesses on the alloys were less than produced under similar conditions on pure nickel or pure cobalt, with the thinner coatings being apparently attributable to the slower rates of solid state diffusion of aluminum in the superalloys compared to pure nickel and cobalt. Nevertheless, obtaining of any significant coatings on such materials at temperatures as low as 1000° F. (and they are usually coated at above 1500° F.) is a clear indication of the accelerating effects on conventional aluminizing techniques produced by the accelerator additions in accordance herewith.

For purposes of clarity or explanation, as will be understood, and to make comparable the various data and limits indicated above, the various specific examples heretofore noted have all been treated utilizing substantially the same aluminizing pack with the various noted accelerating additions. It is to be understood as comprehended within this invention, however, that various other coating packs and operating conditions, as well known in this art, may be utilized for the diffusion coating or deposition of coating materials (such as the aluminum and antimony coatings noted above) into a variety of different metal articles, while still obtaining the accelerating benefits of the pack additions in accordance herewith. For example, the aluminum metal content of packs may be varied widely between about 10% and 95% by weight and still produce good quality coatings, particularly on ferrous base materials. The amount of aluminum deposited increases with the aluminum content of the pack, and is affected by other factors well known in this art, but, as noted above, the quantity of depositions appears substantially not to be a function of the accelerator concentration provided the latter is at least about 0.25% of the pack. As well understood, packs containing no more than about 5% aluminum produced rather thin coatings, whereas packs containing over 50% aluminum produced thick coatings that exhibited excessively rough surfaces. In any event, a range of about 20% to 30% by weight of aluminum in the pack is generally preferred from the practical standpoint of coating quality, although acceleration of aluminum deposition in accordance herewith is achieved at virtually any practical concentration of aluminum metal in the coating pack.

As previously noted, varying the accelerator content between about 0.5% and 5% by weight of a 20% aluminum pack had virtually no significant effect on the amount of the aluminum deposited. When as much as 2–5% lead or cadmium was used as the accelerator, however, the coatings produced had a tendency to exhibit surface contamination by the accelerator material, being manifest as a physical "stick-on" producing less than optimum appearance and substantial surface roughness. Reducing the accelerator content below 0.25%, on the other hand, also produced a reduction in the rate of aluminum deposition and/or degree of acceleration thereof, which became virtually unobservable below 0.125%.

Thus, as noted, a preferred concentration from a practical point of view for the accelerator is about 1% by weight of the pack. Despite the foregoing, however, very satisfactory results have been achieved in accordance herewith with the metallic accelerator component comprising 1% of cadmium together with 1% of lead or 1% of zinc, and the coatings produced thereby were substantially free of "stick-on" with good surface appearance, low surface roughness, and a thickness of aluminum deposition optimumly accelerated for a given time-temperature cycle, at least at temperatures above 850° F. as noted above depending upon variations in the particular substrate or metal articles being coated.

Variations in the range of halogen energizer appear not to be controlling as to the accelerator techniques hereof. Generally, the energizer concentration (considered as ammonium halide) should be maintained at or above about 0.25% by weight of the pack. The amount of aluminum deposited from a 20% aluminum pack containing 1% cadmium accelerator may increase as much as five-fold if the ammonium iodide content is increased from 0.25% to 0.5%, although the amount of aluminum deposited even at the 0.25% level was still greater than that achieved in comparable packs without the accelerator additives.

Similarly, when zinc is to be coated along with aluminum, including about 0.5% ammonium halide in the pack is preferred for moderately alloyed steels such as AMS 5616, as well as with 17–4 PH stainless steel alloys, although, with the latter, the amount of zinc ultimately included in the coating was decreased by raising the energizer level to 1%, probably because of an increase in the amount of aluminum which the higher energizer level supplied to the surface of the article. With low alloy steels, such as AMS 6304, which exhibited a more rapid solid state diffusion rate for zinc, a 1% halide content may be preferred to prevent excessive zinc deposition from the pack prior to aluminum deposition.

Again, for enhanced clarity of disclosures and to keep the various specific examples and data noted above comparable, the results discussed heretofore have involved utilizing one or more of the metals calcium, lead, tin, or zinc as the accelerating additive, primarily for purposes of illustration, in enhancing the deposition of coating materials such as aluminum or antimony, at relatively low temperatures (no more than 1000° F.) in the diffusion coating of base meltal articles or alloys composed primarily of iron, chromium, nickel, cobalt, titanium, etc., and using coating packs which, prior to the accelerating addition, are generally conventional in utilizing any one of the four halogens, or halides thereof, as diffusion energizers and alumina as an illustrative inert filler—all in known and well understood manner.

It has also been discovered, however, and is to be understood as comprehended within the teachings hereof, that satisfactory results are achieved in accordance herewith by the utilization of certain organic compounds as the accelerating additives to coating packs, as well as the accelerating metals noted above. Generally, satisfactory results have been achieved utilizing a variety of long chain alcohol and/or fatty acid compounds present in concentrations of about 5—10% by weight of the pack as accelerating additions resulting in up to a five-fold increase in the deposition rate of the coating metals into the surface of the article being coated at treating temperatures around 1000° F.

As will be understood, a wide variety of such organic compounds is available, and the selection of any particular one is readily made in accordance herewith and from the teachings hereof without inventive experimentation. Merely as illustrative, satisfactory results have been achieved by utilizing such materials as glycerol, butanol, and lauric acid added to powdered packs containing about 20% aluminum, 0.5% ammonium iodide, and alumina as a filler, to achieve concentrations of the organic hydroxy materials in the pack of about 5% to 10% by weight. Although such organic accelerators may be incorporated in the powdered packs in a variety of ways, satisfactory results have been achieved in accordance herewith by admixing (for example, in a ball mill) into the pack powder a solution of the organic accelerator dissolved in an appropriate solvent (such as ethanol) and then removing excess solvent by evaporation, drying, or vacuum, prior to utilizing the pack. Other means of uniformly distributing the organic accelerator throughout the powdered pack composition will be apparent from the disclosure hereof by men skilled in this art.

The selection of the particular organic material appropriate for use as an accelerator in connection herewith is readily achieved by noting the discussion above regarding the provision of an accelerating material which, being otherwise not incompatible with the metallurgical requirements of the coating process, has the effect of increasing the kinetics of decomposition of the complex or compound formed in the pack between the coating metal and the halogen energizer utilized to transfer the coating metal to the article being coated for diffusion of the metal into the substrate to be coated at the temperatures desired with due regard to the thermodynamic stability of the compounds, etc. Thus, organic materials having a reactive hydroxy group (to liberate a reducing hydrogen ion), a large enough molecule in addition to the hydroxy radical to have a relatively high decomposition temperature (generally within the range of the coating temperatures desired), and a low volatility produce satisfactory results in accordance herewith.

With relatively heavy alcohol or fatty acid materials having decomposition temperatures as desired, the organic accelerator is thermally decomposed during the coating operation to liberate reducing hydrogen in situ in the coating pack enclosed in the coating retort. This reducing hydrogen, then, effectively reduces the halide of the coating metal (for example, aluminum tri-iodide) to present the coating metal to the substrate in vapor phase or other reactive condition for diffusion into the surface of the article being coated—substantially in the manner discussed above for the reduction of aluminum tri-iodide by the zinc or cadmium or other metallic accelerator additives in accordance herewith, thus to increase or concentrate or accelerate the kinetics of presentation of diffusable coating material to the surface of the article being coated at the desired low coating temperatures and/or within the desired shortened coating reaction times.

As will be understood, within the foregoing general disclosures, particular organic materials, in addition to those specifically noted above, are readily selected to function thermodynamically to achieve the coating acceleration results in accordance herewith. Indeed, although many of the physical and chemical properties of organic materials are generally thought to be inimical to the utilization of such materials as active ingredients in high temperature metal lurgical techniques such as those to which this invention relates, the organic accelerators may be preferred in many applications of this invention even to the metallic accelerators mentioned above since, even in vapor phase, the organic materials may be selected to be less toxic and noxious than, for example, cadmium or lead vapors, especially with large scale commercial mass production installations.

Accordingly, as will be apparent from the foregoing, there are provided in accordance herewith a variety of materials and techniques for effecting an acceleration of the rate of deposition or diffusion coating of such coating metals as aluminum, antimony, etc., in pack cementation diffusion coating techniques for a variety of metal articles or substrates including those predominantly rich in iron, chromium, titanium, nickel, cobalt, etc., by the utilization of such metallic accelerators (either in elemental form or as compounds) as cadmium, lead, zinc, tin, etc., or organic accelerators, for achieving enhanced deposition and/or coating thicknesses, either at lower temperatures than those at which such diffusion coatings are conventionally achievable and/or to achieve greater deposition in less time than by conventional techniques. Such enhanced results are achieved merely by the inclusion or addition in a conventional powdered coating pack of an accelerator additive and, particularly, one which, whether metal or organic, decomposes or reacts during the coating step to accelerate decomposition of the halide of coating material conventionally formed for the transition thereof as a diffusion coating into the substrate being coated and/or otherwise enhance the thermodynamics or kinetics of the coating reaction.

While the methods and compositions set forth above form preferred embodiments of this invention, this invention is not limited to these precise methods and compositions, and changes may be made therein without departing from the scope of this invention which is defined in the appended claims.

What is claimed is:

**1.** In an improved method for diffusion coating of a coating metal selected from the group consisting of aluminum and antimony into the surface of a base metal article composed of a metal selected from the group consisting of chromium, cobalt, iron, nickel, titanium, and alloys thereof, by a pack cementation diffusion coating process in which said metal article is heated as embedded in a powdered cementation coating pack containing said coating metal and a vaporizable halogen energizer for presenting said coating metal to the surface of said article for diffusion thereinto, the improvement of accelerating the diffusion coating of said coating metal onto said article providing increased rate of deposition of said coating metal at a given coating temperature and a decreased coating temperature for a given rate of deposition of said coating metal to said article, which comprises the steps of including in said cementation coating pack an effective amount of an accelerator component for enhancing the kinetics of presentation of said coating metal by said energizer to said surface of said article to be coated for deposition thereon and diffusion coating thereinto, said accelerator component being selected from the group consisting of at least one of the metals cadmium, lead, tin and zinc, which are substantially volatile at said coating temperatures but not susceptible of diffusion coating into said article along with said coating metal, and heating said article to be coated and said coating metal and said accelerator component in said cementation pack effecting said accelerated diffusion coating of said coating metal into said article at said reduced temperature and at said enhanced rate of deposition.

**2.** A method as recited in claim **1** in which said accelerator component is present in said cementation pack within the range of about 0.25% to 5% by weight of said pack.

**3.** A method as recited in claim **1** in which said diffusion coating of said article to be coated is conducted in said cementation coating pack with said accelerator component included therein at a coating temperature at least about 200° F. lower than the same amount of the same coating metal could be diffusion coated into the same metal article without said accelerator component in said pack.

**4.** The method of claim **1**, wherein said base metal article is a ferrous base metal.

**5.** The method of claim **1**, wherein said ferrous base metal is steel.

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