METAL PLATING PARTICULATED SUBSTRATES
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ABSTRACT OF THE DISCLOSURE
Process for metal plating a particulated substrate by preparing a heated solvent slurry of the substrate under
inert conditions and introducing a heat-decomposable
metal plating compound into the heated slurry while pro-
viding agitation of the slurry and reflowing of the solvent
vapors.

CROSS REFERENCE TO RELATED APPLICATION
This application is a continuation-in-part of application

BACKGROUND OF THE INVENTION
Solution plating as practiced in the art today generally
comprises immersion of a hot substrate in a solution of
a heat-decomposable metal compound. There are many
advantages to solution plating employing heat-decom-
posable metal compounds to prepare high purity coatings.
Among the attendant advantages of solution plating is
that corrosion or oxidation of the substrate is greatly
minimized both before and during the coating operation.
Another chief advantage of solution plating is its simplicity
and the economical attractiveness of the high utilization
of the heat-decomposable metal compound which gener-
al represents a significant portion of the cost of metal
plating utilizing such materials. A serious limitation of
solution plating, however, is its lack of suitability for
plating substrates characterized by having a high heat
transfer rate or low heat capacity, for example, see U.S.
Pats. 2,523,461 and 3,041,197. The problem with such a
substrate is that its contained heat as well as heat con-
tinually imparted to it is so rapidly conducted away and
absorbed by the solution that little or no plating occurs.
In other words, the substrate is rapidly cooled below the
temperature of decomposition of the heat-decomposable metal compound contained within the
plating solution so that the process is generally restricted
to the deposition of relatively thin coatings. The problem
is not solved by simply increasing the heat input to the
substrate because this leads to unfavorable side effects,
such as decomposition of the compound away from the
surface of the substrate and/or the formation of a loose
nodular deposit. Moreover, there are many substrates hav-
ing certain properties either inherent or imparted thereto
which are altered or destroyed upon heating to an elevated
temperature, e.g., metal powders having magnetic prop-
erties which are destroyed upon heating to elevated tem-
peratures. The problems discussed above naturally result
in a less efficient utilization of the heat-decomposable
metal compound and impose a subsequent separation step
to remove any decomposed free metal existing in the final
product. The above disadvantages associated with solution
plating as practiced in the art today makes coating of
particulated substrates having a high surface area to mass
ratio especially impracticable. Therefore, a low tempera-
ture process for the solution plating of particulated sub-
strates, especially with more efficient utilization of the
heat-decomposable metal compound, would represent a
welcome contribution to the art.

SUMMARY OF THE INVENTION
The present invention provides a process for metal
plating a particulated substrate, said process comprising
in combination preparing a slurry of said particulated
substrate in a thermally stable organic solvent essentially inert
under process conditions and capable of dissolving a heat-
decomposable metal compound selected from the group
consisting of trisobutylaluminum, triisobutylaluminum hy-
dride, tris(hexamethyldisilazane) aluminum, triisobutylal-
ylene aluminum, diisobutylaluminum hydride, and di-
ethylaluminum, heating the prepared slurry in a system
under substantially inert conditions to at least the decom-
position temperature of said heat-decomposable metal
compound, and introducing said heat-decomposable metal
compound into the heated prepared slurry.

DESCRIPTION OF THE DRAWING
The drawing depicts a schematic apparatus arrangement
wherein a preferred embodiment of the present process can
be conducted.

DESCRIPTION OF THE PREFERRED
EMBODIMENTS
The present invention provides a process for metal
plating a particulated substrate comprising preparing a
slurry of the particulated substrate in a solvent capable
of dissolving a heat-decomposable metal compound, heat-
ing the substrate-solvent slurry in a system under inert
conditions to at least the decomposition temperature of
the heat-decomposable metal compound, and incremental-
ly introducing the heat-decomposable metal compound
into the heated substrate-solvent slurry while continuously
agitating the slurry. In this manner, the particulated sub-
strate is expeditiously coated at a high degree of effi-
ciency.

By incremental addition of the plating compound to the
substrate-solvent slurry is meant addition at a rate suf-
cient to avoid excessive build up in concentration in the
slurry, that is, opposed to a system where all of the plating
compound is added initially. The heat-decomposable metal
plating compound is preferably added to the particulated
powder-substrate slurry at a rate sufficient to decompose
the compound almost essentially instantaneously upon
contact with the slurry. Generally, for most operations it
can best be described as dripping the plating compound
into the slurry. However, it is to be understood especially
in the case of a large slurry mass, that the compound can
be added in a larger volume over a continuous basis.

Addition of the plating compound to the slurry is
regulated depending upon the ratio of substrate to solvent
present, the mixing speed (that is, the rapidity at which
each individual substrate member is brought into position
and exposed to the plating compound), and the selected
temperature for plating. Under these conditions.

Among the outstanding features and advantages of the
instant invention is the fact that the thermal decomposi-
tion of heat-decomposable metal compounds in the above
manner is primarily a surface catalyzed reaction such that
decomposition proceeds at a temperature reduced below that normally required for decomposition of the specific heat-decomposable compound at the particulated substrate surface whereby a continuous, adherent, coherent coating is realized thereon. By controlling the process to effect a surface catalyzed reaction, deposition on non-substrate surfaces, such as the walls of the reactor, or in the solvent to produce free aluminum particles, is avoided. Moreover, it will be seen as the discussion proceeds that it is not necessary nor desirable to directly heat the substrate in order to decompose the heat-decomposable metal compound, but rather, the necessary heat can be supplied simply by heating the solvent to the preferred process temperature.

It is preferred to conduct the present process in a system under reflux conditions utilizing a solvent having a boiling point less than the temperature at which the heat-decomposable metal compound is normally decomposed but at least as great as the reduced temperature at which decomposition of the compound proceeds by a surface catalyzed reaction. Solvents having a boiling point greater than the normal decomposition temperature of the heat-decomposable metal compound can be used in an application wherein some solvent decomposition of the metal compound can be tolerated, for example in the coating of magnetic powders which are subsequently compacted into a specific geometry, the main function of the coating being to serve as a binder so that some free metal can be tolerated. Reflux conditions are preferred since by continually cooling the solvent vapors and returning them to the slurry, the temperature of the substrate-solvent slurry is conveniently regulated.

Referring now to the drawing, the particulated substrate-solvent slurry 10 contained in the vessel 11 is heated by heating means 12 and continually stirred or agitated by means, such as the mixing means 13. When the substrate-solvent slurry 10 reaches the temperature at which the heat-decomposable metal compound is to be decomposed as indicated by the temperature indicating means 14, the plating compound 15 is then incrementally added via the conduit means 16 to the substrate-solvent slurry by regulation of the valve means 17. The plating compound is preferably brought into contact with the substrate-solvent slurry 10 in the close vicinity of the mixing means 13, e.g. in the vortex created thereby. This procedure insures rapid and efficient contact between the substrate and the plating compound. It is to be understood of course, that under refluxing conditions it is not mandatory to employ the mixing means 13 since sufficient agitation can be achieved by ebullition of the solvent. As the substrate-solvent slurry 10 is heated, vapors 18 flow toward and upon contact with the condensing means 19 are condensed and returned to the slurry. Any by-product gases produced are allowed to pass out of or are swept out of the system by thermal diffusion or with an inert carrier gas through the liquid bubbler means 20 via the line 22 wherein the valve means 23 is positioned. In this manner, the system is operated at essentially atmospheric pressure as would be indicated by the pressure gauge 21. The conduit 24 and valve means 25 are provided for purging and/or filling the vessel 11.

It can be appreciated that considerable variations can be made in the apparatus arrangement depicted in the drawing without departing from the true spirit and scope of the present invention. For example, the plating compound 15 can be introduced directly within the substrate-solvent slurry itself by immersing the conduit means 16 therein. Moreover, the substrate-solvent slurry 10 can be agitated by an inert gas introduced beneath the surface thereof and which gas can include vapors of the selected heat-decomposable metal compound. Additionally, automated components can be employed in the system and the operation conducted on a continuous basis.

The instant process is not limited by any particular size or geometry of substrate as long as it is capable of being mixed with a solvent to form a slurry. Moreover, the substrate must be capable of withstanding the requisite temperature to decompose the heat-decomposable metal compound, the only restriction being that it must be compatible with the solvent. Substrates employed herein can best be described as particulated materials, e.g. powders, pellets, small fasteners, and the like. Such finely comminuted materials are generally characterized as having a high heat transfer rate to the extent that they cannot be readily plated, if at all, by conventional solution plating techniques. Particulated metals, metal alloys, oxides, and carbides are especially preferred since these materials, heretofore difficult to plate by conventional solution plating, are characterized by their excellent heat stability, plus the fact that unique articles of manufacture as hereinafter described are readily produced by way of the present process. However, other particulated materials, such as glass, ceramics, refractories, graphite, etc., can likewise be employed. The present process provides efficient plating of such substrates at low temperatures regardless of their particular size or configuration as long as they can be slurried. The instant process is, however, particularly attractive for coating particulated substrates having an average particle size less than about 50 microns, e.g. fine particle magnets comprising an iron-cobalt alloy which materials cannot be heated above 200° C. for extended periods of time without losing their special magnetic properties. Such materials when coated by the instant process utilizing a heat-decomposable aluminum compound and dispersed in a non-magnetic matrix (e.g. aluminum) can be formed into a high coercive force permanent magnet.

Preferred heat-decomposable plating compounds are (A) metal hydrides and their complexes having the following formulas:

(I) \[ M \text{H}_3 \text{ or M} \text{H}_4 \text{Ligand} \]

and

(II) \[ \text{R}_m \text{M} \text{H}_n \]

wherein M is a metal atom, R is an alkyl or aryl group, H is hydrogen, and m and n are small whole integers ranging from 1 to 4, and (B) organometallic compounds having the following formulas:

(III) \[ \text{R}_m \text{M} \]

wherein R is an alkyl, aryl, arene, cyclopentadienyl, cyclopentadiene, alkaryl, or aralkyl radical, M is a metal atom, and m is a small whole integer ranging from 1 to 5, and

(IV) \[ \text{R}_m \text{MX}_y \]

wherein R and M are defined as above and X is selected from the group consisting of carbonyls, nitrosyls, phosphines, and mixtures thereof, and m and y are small whole integers ranging from 1 to 4, and

(V) \[ \text{M(CO)}_m \text{ or M}_2 \text{(CO)}_n \]

and

(VI) \[ \text{M(CNR)}_m \]

wherein M is a metal atom, R is hydrogen, an alkyl, or aryl radical, m is a small whole integer ranging from 4 to 6, x is a small whole integer ranging from 2 to 4, and the ratio n/x ranges from 3 to 5 and

(VII) \[ \text{M(CO)}_m \text{(NO)}_n \]

wherein M is a metal atom and m and n are small whole integers ranging from 1 to 3.
Exemplary of suitable compounds are: silane, stan-
nane, diethylaluminum hydride, disobutylaluminum hy-
dride, trimethylamine, tertiary amine alanes in-
cluded trimethylamine, bis(trimethylamine)alane,
tris(dimethylamine), triisopropylamine, tri-n-butyl-
aniline, and tri-n-sec-butylamine, disobutylberyl-
lium, di tert-butyllium, diethylmagnesium, di tert-
butylmagnesium, diethylzinc, diethyldiamine, triethyl-
borane, triethylaluminum, triisobutylaluminum, diethyl-
tin, tetrachloroethylene, dibenzen zinc, dimethyl-
chloride, bisdimethyl amine, dimethylaniline, tetra-
ylenc isobutylene, dicumene tungsten, bis-cyclopentadi-
enytitanium, bis-cyclopentadienylmanganese, bis-
cyclopentadienyliron, bis-cyclopentadienyl nickel, cumene chlo-
rium dinitroxy, benzene molybdenum tricarbonyl, cyclo-
pentadienyltitanium dicarbonyl, cyclopentadienylichromi-
ium tricarbonyl, cyclopentadienylnitrate, cyclopentadienyl-
olefins, silicone oils, ketones, and the like. From a cost-effectiveness standpoint, aromatic hydrocarbon sol-
vents are preferred for use in this invention, such as:
toluene, xylene, mesitylene, decalene, and the like.

Exemplary of suitable solvents are kerosene, Primol-
D (an essentially aliphatic hydrocarbon solvent), hexane,
benzene, toluene, xylene, alpha-methyl-naphthalene, beta-
methyl naphthalene, 1,4-dimethyl naphthalene, decahydro-
naphthalene, 1-ethyl-3-methyl benzene, 1-ethyl-4-methyl-
benzene, isopropyl benzene, alpha-methoxy toluene,
1-methyl-2-propyl benzene, 1-ethyl-3-propyl benzene, 1-
methyl-4-propyl benzene, 1,2,3,4-tetrahydro naphthalene,
pentane, heptane, decane, nonane, octane, cyclopentane,
cyclohexane, methylecyclohexane, poly methylsiloxane,
methyl methacrylate, dibutyl ketone, ethylene glycol di-
methyl ether, ethylene glycol diethyl ether, propylene gly-
col dimethyl ether, diphenyl ether, anisole, propyl ether,
tetrahydrofuran, diethyl glycol dimethyl ether, and mix-
tures thereof, such as might be found in petroleum dis-
tillates.

In order that those skilled in the art can thus appreciate the process of this invention, the following exam-
pl es are given by way of description and not by way of limitation. In the examples, the apparatus arrangement shown in the drawing was employed. The heating means 12 consisted of an electric resistance heater. A conven-
tional electrically driven mixer was employed as the mixing means 13. The slurry 10 consisting of the particulated substrate and solvent was charged into the vessel 11 which had been previously purged with nitrogen through line 24 to rid the system of air and moisture. In those instances where the slurry 10 was thought to contain traces of moisture, the startup procedure comprised first heating the slurry 10 so as to distill off a small amount of solvent and co-distill any traces of moisture which was allowed to escape from the vessel 11 through the line 22 to the bubbler means 20. Thereafter the condenser means 19 was set into operation by opening the valve means 26 which allowed cooling fluid to move through the means 19. Concurrently, the mixing means 13 was set into opera-
tion and the heater means 12 adjusted so as to heat the slurry 10 to the temperature employed for decomp-
sing the particular heat-decomposable metal compound employed in each specific instance enumerated below. By virtue of the temperature indicating means 14 the op-
erator could observe and regulate the temperature during the plating operation. When this temperature reached the librium, that is, the flow rate of the solvent vapors 18 was equal to that of the solvent 27 refluxed back to the slurry 10 by controlling the extent of cooling via the cooling means 19 (for the preferred method of operation), the system was then ready to commence plating. Under these conditions the pressure gauge 21 read essen-
tially atmospheric pressure.

The plating compound was incrementally added through the conduit means 16 as controlled by the valve means 17 to the agitation slurry 10 by dripping it into the vortex created by the impeller of the mixing means 13. In the following runs, where a solid plating compound was used the compound was initially dispersed in the same solvent as that employed to prepare the particulated powder-sub-
strate slurry. Where liquid compounds were used, a sim-
ilar solvent system was employed. However, it is to be understood that the pure plating compound itself can be utilized.

EXAMPLE I

Substrate—Magnetic Alloy Powder

Plating compound—Disobutylaluminum—(C2H5)2Al

Solvent—Dodecane

Temperature of slurry—195° C.

Results—Gray metallic coating encapsulating individual agglomerates of alloy powder.
EXAMPLE II
Substrate—Magnetic Powder
Plating compound—Trimethylamine alane—AlH₃·Me₃N
Solvent—Xylene
Temperature of slurry—140° C.
Results—Gray metallic coating encapsulating individual agglomerates of alloy powder.

EXAMPLE III
Substrate—Glass fibers
Plating compound—Trimethylamine alane—AlH₃·Me₃N
Solvent—Xylene
Temperature of slurry—140° C.
Results—Dull gray aluminum deposit coating individual particles of glass fibers.

EXAMPLE IV
Substrate—Magnesium oxide—MgO
Plating compound—Chromium hexacarbonyl—Cr(CO)₆
Solvent—Octadecane
Temperature of slurry—300° C.
Results—Chromium coated MgO for compaction into massive metal with improved ductility.

EXAMPLE V
Substrate—Submicron thorium oxide—ThO₂
Plating compound—Nickel tetracarbonyl—Ni(CO)₄
Solvent—Xylene
Temperature of slurry—120° C.
Results—Thoria dispersed nickel powder for conversion to dispersion strengthened nickel parts.

EXAMPLE VI
Substrate—Nickel powder
Plating compound—Cyclopentadienyltantalum tetra carbonyl—CyTa(CO)₄
Solvent—Decalin
Temperature of slurry—195° C.
Results—Tantalum coated nickel powder for compaction and heat treatment to produce Ni-Ta alloy for high temperature applications.

EXAMPLE VII
Substrate—Beryllium powder
Plating compound—Diisobutylaluminum hydride—(C₈H₁₈)₂AlH
Solvent—Dodecane
Temperature of slurry—210° C.
Results—Aluminum coated beryllium powder for compaction into light, ductile metal with high strength-to-weight rates.

EXAMPLE VIII
Substrate—Magnetic powder
Plating compound—Cyclopentadienylicopper triethylphosphine—CyCu(Et₃P)
Solvent—Decalin
Temperature of slurry—195° C.
Results—Copper coated magnetic powder for fabrication into corrosion-resistant magnetic parts with high coercive force.

EXAMPLE IX
Substrate—Lead oxide
Plating compound—Tetraethyllead—Et₄Pb
Solvent—Dodecane
Temperature of slurry—126° C.
Results—Dispersion-hardened Pb alloy.

EXAMPLE X
Substrate—Graphite
Plating compound—Cyclopentadienyltitanium dicarbonyl—CyTi(CO)₂
Solvent—Octadecane

Temperature of slurry—300° C.
Results—Titanium coated graphite for fabrication into electrodes of improved oxidation resistance.

The amount of coating to be deposited pursuant to the present process will vary with the type of substrate and its subsequent application. In general, for most applications the coating is a minor constituent of the finished product, that is, thin coatings are generally suitable. Preferably, coating buildup ranges upwards to 50 volume percent based upon the finished coated product. It is to be understood that the finished product can contain or include any free metal (constituting the metal constituent of the plating compound) that is formed during the coating operation. In fact, there are instances where free metal can be present in the end product in considerable amounts without detrimental effect. For example, in the case of coated magnetic powders utilized in the preparation of permanent magnets. The free metal (plating metal) together with the coated particulate substrate can be fabricated by conventional metallurgical techniques into the desired magnet whereby the free metal serves as a matrix wherein the particulated substrate is suspended.

A preliminary step prior to employing the technique of this invention may desirably require surface preparation of the substrate to be plated. However, a feature of the present invention is that preliminary surface preparation is not mandatory in the case of many substrates as they are commercially supplied since they are continually contacted and mixed with the solvent during the plating operation. Where it is desired to implement the present technique with a surface preparation step many well known methods of surface preparation can be employed. For example, degreasing followed by acid pickling and washing is one suitable approach.

Particulated materials coated pursuant to the present invention find diversified uses both as individual components as well as intermediate components that can be further fabricated into unique articles of manufacture. For example, appropriate base materials can be coated with materials such as nickel or the like to form catalysts. Pursuant to the preferred embodiment of the instant invention, appropriate metal powders can be initially coated with aluminum which when subjected to conventional metallurgical techniques will serve as an appropriate binder. Of special interest is the use of an aluminum coating deposited by the instant invention on particles of iron-cobalt alloy, the aluminum serving as a binder for the particles in the preparation of permanent magnetic materials and also for the protection of the parts against oxidation, and corrosion conditions. The instant invention is also attractive for the coating of glass fibers, the coating serving to minimize deterioration of the glass fibers against subsequent loss in strength due to aging. Moreover, the present invention represents excellent means for preparing special alloys by depositing special coatings on ultra-fine metal powders.

It is to be understood that the present invention is not limited by the specific embodiments described hereinabove, but includes such changes and modifications as may be apparent to one skilled in the art upon reading the appended claims.

We claim:

1. A process for metal plating a particulated substrate, said process comprising in combination:
   (1) preparing a slurry of said particulated substrate in a thermally stable organic solvent essentially inert under process conditions and capable of dissolving a heat-decomposable metal compound selected from the group consisting of trisobutylaluminum, diisobutylaluminum hydride, and trimethylamine, and
   (2) heating the prepared slurry in a system under substantially inert conditions to at least the decomposition temperature of said heat-decomposable metal compound, and
   (3) introducing said heat-decomposable metal com-
3,549,412

9. The process of claim 1 wherein the substrate comprises small fasteners.
10. The process of claim 7 wherein said compound is introduced incrementally.

11. The process of claim 7 wherein the heating step produces solvent vapors which are refluxed as a means of controlling the temperature of the substrate-solvent slurry.
12. The process of claim 7 wherein the substrate comprises a powder.
13. The process of claim 7 wherein the substrate comprises pellets.
14. The process of claim 7 wherein the substrate comprises fibers.

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