April 23, 1963 W. C. JENKIN 3,086,881

METHOD FOR SECURING ADHESION OF GAS PLATING

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FIG-1

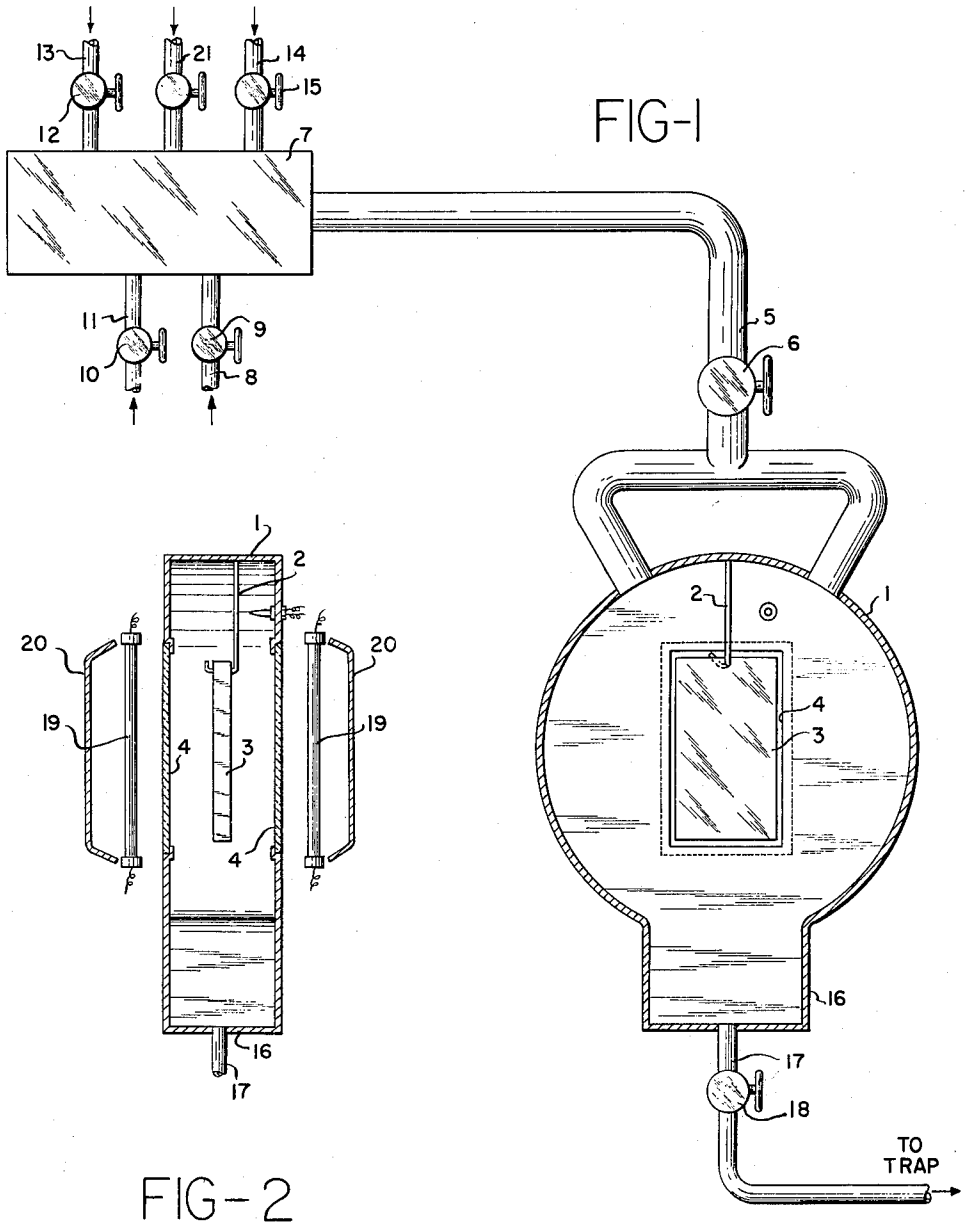


FIG-2

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METHOD FOR SECURING ADHESION OF GAS PLATING

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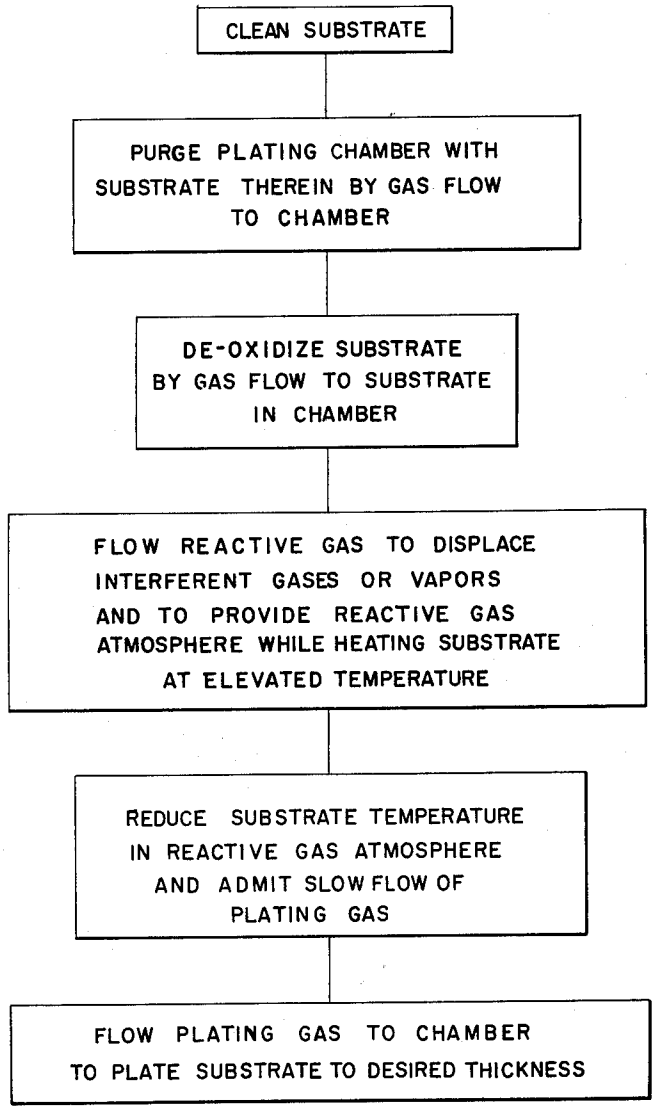


FIG-3

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METHOD FOR SECURING ADHESION OF GAS PLATING

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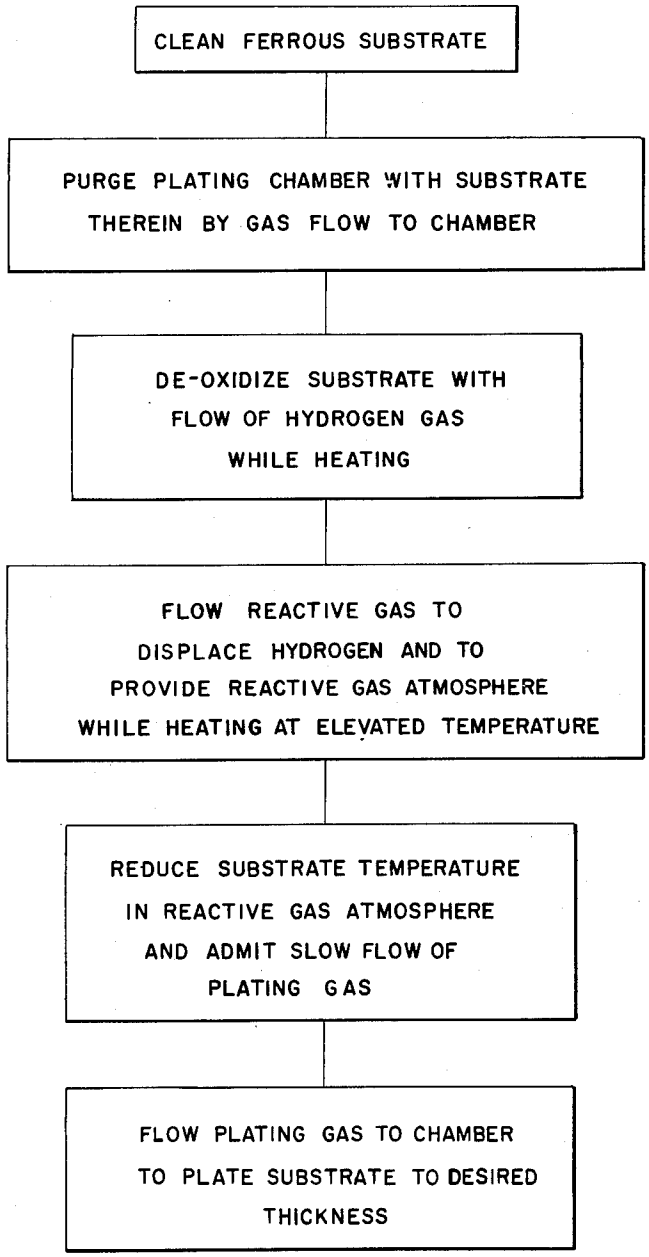


FIG-4

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METHOD FOR SECURING ADHESION OF GAS PLATING

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10 Claims. (Cl. 117—50)

This invention relates to the plating of metals from gases or vapors, and in particular is concerned with attaining good adhesion between a substrate and a deposit of metal in a novel manner.

Customarily high degrees of adhesion of a metal plate or deposit have been achieved by resort to vacuum degassing of the substrate prior to subjecting the substrate to the plating gas or vapor. While such procedure is effective it involves relatively low pressures—as low as 1 mm. of mercury—and this entails the use of equipment capable of producing the high degree of vacuum as well as apparatus capable of withstanding the pressures involved in such vacuum operations. Further, such procedures are time consuming, materially increasing plating cost.

This present invention contemplates the provision of a process which eliminates the necessity for vacuum operation while yet providing adhesion between a substrate and deposited metal and which adhesion is equivalent to that obtained with vacuum operations. Further, the process of invention is useable under vacuum conditions of plating if so desired though such is not necessary and would provide no particular advantage.

In the practice of the present invention heat decomposable metal bearing carbonyl gases are employed to obtain the metal deposit. A plurality of such gases are known, the more common being nickel carbonyl, iron pentacarbonyl and chromium hexacarbonyl. These gases from which the metal is derived by heat decomposition of the gas are illustrative with respect to the practice of the invention.

The substrates to which the metal or metals, derived by heat decomposition, are applicable, cover a wide range of materials—metals, plastics, glass and ceramics. In fact, the invention is utilizable in conjunction with the plating of substrates which tend to adsorb gases of any kind—most materials, such as those listed, either in exposure to the atmosphere or in the course of cleaning, acquire on their surfaces some adsorbed gas, such as hydrogen, water vapor and gases of the air, which interfere with good adhesion in the plating process. Such adsorbed gas may accordingly be termed as interferent.

However, the invention finds its present greatest utility in connection with the plating of ferrous metals, such as iron, carbon steel, alloy steels and the like, wherein the tendency of the substrate is to take up such interferent gases which tenaciously adhere to the substrate and are displaced only with difficulty and apparently somewhat incompletely in customary preparation procedures.

Removal of the interferent gas or vapor is accomplished in the practice of the present invention by displacing the interferent with a gas or vapor atmosphere which is reactive with the gaseous heat decomposable metal bearing compound. This is effected by exposing the substrate with adsorbed interferent gas thereon to the reactive gas atmosphere. The displacement of the interferent is aided by heating of the substrate during the exposure. The effect of the introduction of the reactive gas atmosphere is apparently to upset the molecular forces holding the interferent on the substrate thereby permitting the interferent to escape.

It is considered that the interferent would be upset by

the heat decomposable gas itself if the substrate were subjected to such heat decomposable gas with the interferent thereon. Then the escaping interferent would obstruct the entry of the heat decomposable gas to the surface of the substrate and a high degree of adhesion is inhibited.

By providing in the place of the interferent adsorbed gas a gas atmosphere which is reactive with the plating gas—the entry of the plating gas or heat decomposable gas to the surface of the material to be plated is unobstructed and adhesion comparable to that of high vacuum processes is obtained. Accordingly the invention contemplates as an essential procedural step the exposure of a substrate to a reactive gas prior to the introduction to the substrate of the heat decomposable metal bearing gas whereby the reactive gas is itself removed from the substrate surface by reaction with the entering plating carbonyl.

Where the substrate is iron or a carbon steel which has been cleaned of oxide by exposure to hydrogen some of the hydrogen is adsorbed; the reactive gas found most suitable in such instance is a mixture of dry ammonia and carbon monoxide. Carbon monoxide alone, however, is not satisfactory in the metallizing of ferrous substrates to attain optimum adhesion, apparently because carbon monoxide itself is adsorbed tenaciously at the surface of such substrates.

Ammonia alone in connection with the treatment of ferrous substrates particularly tends to result in a brittle plate; accordingly the ammonia, it has been found, requires some diluent such as the carbon monoxide, nitrogen or other inert gas such as neon or argon.

The reactive gas atmosphere is thus for ferrous metals a mixture of gases and for ferrous base materials the optimum proportion has been found to be about 50 percent by volume of dry ammonia and 50 percent by volume of a second gas. Exceeding 75 percent by volume of the ammonia leads toward embrittlement, while less than 25 percent of ammonia results in decreased adhesion of the ultimate plate.

The effect of ammonia and carbon monoxide appears to be physical in displacement of the interferent gas. The displaced interferent is expelled with other gases from the plating chamber in the course of the preparation of the chamber volume for the metallizing operation.

As a theory the mechanism or rule followed by the reactive gas atmosphere in functioning to provide an improved adherent metal bond is: the reactive gas is taken up by the substrate and when the carbonyl enters the ammonia apparently simply displaces a CO group from $Ni(CO)_4$ and then $Ni(CO)_3NH_3$ a gaseous product is formed. Carbon monoxide displaces a CO group similarly, the resultant product being, of course, the same nickel carbonyl. Proof that such occurs is that CO tagged with a radio active element will displace a CO molecule and the tagged CO group will show up in the nickel carbonyl when the tagged CO is simply in contact with the nickel carbonyl. However, it does not appear that carbon monoxide itself is a primary factor for it may be replaced by nitrogen, for example. Accordingly the primary function of the CO, N_2 or other inert gas is apparently that of a diluent.

From the foregoing it may be seen that the adsorbed reactive gases produce with the plating gas volatile material and further, these materials are themselves heat decomposable to deposit metal. The combined effect of these features is that the substrate is rid of the interferent material and plating commences instantaneously with the introduction of the carbonyl, and adhesion of the plated metal to the substrate is high.

The invention will be more fully understood by refer-

ence to the following detailed description and accompanying drawings wherein:

FIGURE 1 is a view illustrating an apparatus arrangement useful in the practice of the invention;

FIGURE 2 is a side view of apparatus particularly illustrating heating means of the apparatus arrangement;

FIGURE 3 is a flow sheet illustrating steps of the procedure of the invention; and

FIGURE 4 is a flow sheet illustrating appropriate steps of a procedure in the metallizing of a carbon steel object.

Referring to FIGURE 1, the numeral **1** designates a plating chamber having a support element **2** in the form of a hook on which there is suspended a carbon steel plate **3** to be metallized. The numeral **4** designates windows, suitably of a heat resistant material, such as Pyrex glass, and which passes infrared radiation. One window may conveniently be openable to permit insertion in the chamber of objects to be plated.

An inlet conduit **5** is provided with a control valve **6** which is normally open in operation. Communicating with conduit **5** is manifold **7** through which gases pass to the plating chamber. A flow line **8** has a valve **9** for controlling the flow of a de-oxidizing gas, in the present instance hydrogen, through the manifold **7** to the plating chamber.

A valve **10** in conduit **11** controls the flow of the ammonia to the manifold **7**; valve **12** in line **13** controls the flow of carbon monoxide to the manifold for mixing with the ammonia prior to passage of this reactive gas atmosphere to the plating chamber.

A conduit **14** having a valve **15** communicates a source of the plating gas with the manifold. The plating chamber **1** itself has a depending portion **16** through which exhaust gases pass to an outlet conduit **17**. Conduit **17** customarily is connected through valve **18** to a trap (not shown) operating at about atmospheric pressure.

The plating gas employed in the practice of the invention is, as noted, heat decomposable to deposit metal. For the purpose of supplying heat to the substrate banks **19** of infra-red heating units having reflectors **20** are disposed opposite the windows **4** (FIGURE 2). The intensity of the heat applied to the substrate is controlled either by control of voltage applied to the infra-red units, by varying the distance of the heating units from the substrate, or by a combination of both of these factors.

To obtain an adherent nickel coating on the carbon steel object **3** the steel is first suitably cleaned; this is effected in any convenient manner as by a sandblasting of the substrate followed by treatment in a trichlorethylene bath; however, conventional cleaning process suitable for electrolytic plating may be employed. The cleaning should be such as to remove all salts from the substrate, particularly hydroxides and the like.

After cleaning the substrate is inserted in the chamber. With valve **18** in line **17** open and valve **6** open, a flow of carbon dioxide nitrogen or the like is admitted through conduit **21** to effect expulsion of air from the plating chamber through line **17**. For aid in purging of the air hydrogen may be admitted through valve **9** of conduit **8**.

After the elimination of air any flow of purging gas, such as CO_2 or nitrogen, is stopped while the flow of hydrogen continues. Plate **3** is heated, the flow of hydrogen is continued to insure de-oxidation of the substrate and complete removal of contaminating oxides. In the event that an inert gas is used in eliminating air, hydrogen flows to the plating chamber to displace the inert gas and to simultaneously de-oxidize the plate.

In the presence of the hydrogen the temperature of the carbon steel plate **3** is raised to at least 700° F. min. to aid the de-oxidation procedure. Apparently, however, even at this temperature, adsorbed gases, including the hydrogen, tend to remain on the object **3**. Such adsorbed gases, as already noted, interfere with the subsequent deposition of the metal from the plating gas and accordingly the removal of such interferents is desirable.

To replace the hydrogen atmosphere of the plating chamber **1** the valve **9** is closed and valves **10** and **12** are opened to admit a flow of dry ammonia gas and carbon monoxide. The flow of gas mixture expels the hydrogen and acts to displace adsorbed gases from the carbon steel object also. In any event the interferent gases no longer function to inhibit adhesion when plating commences. Suitably the flow of the reactive gas mixture comprises about 50 percent by volume of dry ammonia and 50 percent by volume of the carbon monoxide. Preferably also this reactive gas flow is provided to an extent sufficient to replace the volume of the plating chamber at least three times. It has been found that such is entirely satisfactory to assure of elimination of the hydrogen and other contaminants which might still remain.

The temperature at the time of introduction of the ammonia and carbon monoxide is at about 700° F. minimum. This temperature minimum at a time of about 15 minutes has been found most suitable for the de-oxidation of the carbon steel object surface. During the exposure of the object to the reactive gas flow, the temperature is dropped to about 500° F., or if desired somewhat lower but not below the decomposition point of the nickel carbonyl.

When the temperature is reduced as indicated the valves **10** and **12** are at least partially closed and valve **15** is opened to provide a flow of nickel carbonyl to the plating chamber. The carbonyl flow is at first maintained low to provide a low concentration of the carbonyl in the chamber, less than 5 percent of the volume. The continued flow of the ammonia-carbon monoxide mixture is not necessary but aids in carrying the carbonyl to the object to be plated. The reactive gas mixture is displaced by the carbonyl to some extent; more importantly ammonia, the carbon monoxide and the nickel carbonyl react at the surface of the carbon steel object **3** and adsorbed ammonia and carbon monoxide are removed from the plate, providing a clean surface for metal deposition. The first deposition, due to the low concentration of the carbonyl, is simply a very thin flash plate. The deposited metal, however, covers the carbon steel object and plating is continued to build a coherent nickel plate to desired thickness. Suitably the temperature is dropped to 375°–400° F. to effect the bulk of the plating. The ammonia flow is shut off just after the flash plate. The carbon monoxide may continue to flow to serve as a carrier gas if desired. Upon completion of plating the object is removed from the plating chamber, the chamber being first flushed with inert gas.

The adhesion attained is excellent; the carbon steel object when formed of a thin strip 1/16 inch thick and with a deposit of nickel of a thickness of 0.002 inch may be bent around a 1/16 inch diameter without descruction of the nickel steel bond.

As a modification of the foregoing exemplary procedure the dry ammonia may be increased in proportion to the carbon monoxide to provide a ratio of 75 percent of ammonia by volume, and similar results will be obtained as to adhesion. However, the nickel plate tends to be less ductile.

As a second modification the proportion of dry ammonia may be reduced to 25 percent by volume with carbon monoxide constituting the 75 percent—in this instance the plate adhesion is adequate to meet the foregoing vigorous test.

As a further variant it has been found that nitrogen may completely replace the carbon monoxide of the foregoing examples and that similar results will be obtained by the ammonia-nitrogen combination and that the same proportions are effective.

In the foregoing examples organic amines may replace the ammonia in the process of effecting a plating; the amines reacting in the same manner as described in connection with the ammonia, that is, replacing CO groups to form a volatile compound. Further, such similar re-

placement occurs when the carbonyls of chromium, iron and the like are employed.

It is, therefore, only necessary that the displacing reactive gas be capable of displacing the interferent and of reacting with the subsequently introduced plating gas to produce a volatile compound; at the plating temperature such volatile compound may be expelled from the plating chamber with undecomposed plating gas and the products of decomposition of the plating gas, or may itself be decomposed to deposit metal at the surface of the plate.

It is to be noted that the process is of particular effectiveness and utility in the plating of substrates which have a considerable affinity for certain gases. Thus irons and steels have a high affinity for carbon monoxide, and therefore the carbon monoxide, which is adsorbed by the ferrous surfaces, tends to interfere with the adhesion of a deposited plate. In contrast copper, which does not take up CO nearly so strongly, does not require in its treatment the reactive gas in order to provide a high adherence between a metal plate and the copper. In fact, CO alone may be used as the atmosphere into which the plating gas is introduced.

It is further to be noted that while CO does adhere to the ferrous substrates the presence of ammonia or the like in the reactive gas is sufficient to apparently overcome the tendency for CO to be retained by the metal.

Nitrogen when combined with the ammonia in reactive gas atmospheres give equivalent results to CO.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

What is claimed is:

1. In a metal deposition process wherein a heat decomposable metal bearing gas is decomposed thermally in contact with a heated substrate to deposit metal on the substrate, the improvement which comprises the steps of displacing from the substrate adsorbed gases by contacting the substrate with a flow of a gaseous atmosphere containing dry ammonia gas admixed with carbon monoxide and which is reactive with the heat decomposable metal bearing gas to produce a volatile, heat decomposable metal bearing compound, and after displacing such adsorbed gases and while the substrate is in an atmosphere of the reactive gas introducing the heat decomposable metal bearing gas to the heated substrate to occasion a metal deposit.

2. In a metal deposition process wherein a heat decomposable metal bearing gas is decomposed thermally in contact with a heated substrate to deposit metal on the substrate, the improvement which comprises the steps of heating the substrate to an elevated temperature well above the thermal decomposition point of the metal bearing gas, introducing to the so-heated substrate a flow of a gaseous atmosphere containing dry ammonia gas admixed with carbon monoxide and which is reactive with the heat decomposable metal bearing gas to displace adsorbed gases from the substrate, and after displacing such adsorbed gases and while the substrate is in an atmosphere of the reactive gas contacting the substrate with the heat decomposable metal bearing gas.

3. In a metal deposition process wherein a heat decomposable metal bearing gas is decomposed thermally in contact with a heated substrate to deposit metal on the substrate, the improvement which comprises the steps of heating the substrate to an elevated temperature well above the thermal decomposition point of the metal bearing gas, introducing to the so-heated substrate a flow of a gaseous atmosphere containing dry ammonia gas admixed with carbon monoxide and which is reactive with the heat decomposable metal bearing gas to displace adsorbed gases from the substrate, after displacing such adsorbed gases and while the substrate is in an atmosphere of the reactive gas cooling the substrate but maintaining

the temperature such that the heat decomposable gas will be decomposed to deposit metal, and contacting the substrate while the substrate is in the atmosphere of the reactive gas with the heat decomposable gas to thereby deposit metal on the substrate.

4. In a metal deposition process wherein a heat decomposable metal bearing gas is decomposed thermally in contact with a heated substrate, the step of pre-treating the substrate to expel adsorbed, occluded gases which interfere with adhesion of deposited metal to the substrate by effecting the expulsion of the adsorbed occluded gases with a gas atmosphere and containing dry ammonia gas admixed with carbon monoxide and surrounding the substrate therewith and which gas atmosphere is reactive with the heat decomposable gas to form volatile and heat decomposable compounds, and introducing to the said gas atmosphere and the substrate surrounded by the gas atmosphere the heat decomposable metal bearing gas, and maintaining the temperature state of the substrate sufficient to effect the expulsion of the adsorbed occluded gases and sufficient to decompose the heat decomposable metal bearing gas upon entry of the heat decomposable gas to the substrate.

5. In a metal plating process wherein a gaseous heat decomposable metal carbonyl is decomposed thermally in contact with a heated ferrous substrate, the steps of heating the ferrous substrate in a chamber in an atmosphere to which the substrate is inert, heating the substrate in such atmosphere well above the decomposition temperature of the metal carbonyl, eliminating the inert atmosphere from the chamber with a flow of a reducing gas about the heated substrate to remove oxides from the substrate, displacing the reducing gas from about the substrate with a flow of a gas containing by volume at least 25 percent of dry ammonia together with at least 25% by volume of a gas selected from the group consisting of carbon monoxide and nitrogen, reducing the temperature of the substrate while in an atmosphere of the latter said gas to a temperature suitable for the decomposition of the metal carbonyl, flash plating the ferrous substrate by providing a low concentration of the gaseous metal carbonyl in the chamber, and thereafter plating the substrate to the desired thickness by flowing the carbonyl to the heated substrate.

6. In a metal plating process wherein a gaseous heat decomposable metal carbonyl is decomposed thermally in contact with a heated ferrous substrate, the steps of heating the ferrous substrate in an inert atmosphere to a temperature of at least 700° F., eliminating the inert atmosphere from the chamber with a flow of hydrogen about the heated substrate to thereby also remove oxides from the subtrate, displacing the hydrogen with a flow of a gas containing by volume between about 25 and 75 percent of dry ammonia together with carbon monoxide gas, reducing the temperature of the substrate while in an atmosphere of the latter said gas to a temperature suitable for the decomposition of the carbonyl, flash plating the ferrous substrate by providing a low concentration of the gaseous metal carbonyl in the chamber, and thereafter plating the substrate to the desired thickness by increasing the concentration and continuing the flow of the carbonyl to the substrate.

7. In a metal plating process wherein a gaseous heat decomposable metal carbonyl is decomposed thermally in contact with a heated ferrous substrate, the steps of heating the ferrous substrate in an inert atmosphere to a temperature of at least 700° F., eliminating the inert atmosphere from the chamber with a flow of hydrogen about the heated substrate to thereby also remove oxides from the substrate, displacing the hydrogen with a flow of a gas containing by volume between about 25 and 75 percent of dry ammonia together with at least 25% by volume of carbon monoxide, reducing the temperature of the substrate while in the latter said gas to a temperature suitable for flash plating with the metal carbonyl, flash

plating the substrate by providing a low concentration of the gaseous metal carbonyl in the chamber, continuing to reduce the temperature of the substrate but maintaining it above the carbonyl decomposition point, and increasing the flow of the carbonyl to the chamber and heated substrate to continue plating of the substrate without interruption.

8. In a metal plating process wherein a gaseous heat decomposable metal carbonyl is decomposed thermally in contact with a heated ferrous substrate, the steps of heating the ferrous substrate in an inert atmosphere to a temperature of at least 700° F., eliminating the inert atmosphere from the chamber with a flow of hydrogen about the heated substrate to thereby also remove oxides from the substrate, displacing the hydrogen with a flow of a gas containing by volume between about 25 and 75 percent of dry ammonia together with at least 25% by volume of nitrogen, reducing the temperature of the substrate while in the latter said gas to a temperature suitable for flash plating with the metal carbonyl, flash plating the substrate by providing a low concentration of the gaseous metal carbonyl in the chamber, continuing to reduce the temperature of the substrate but maintaining it above the carbonyl decomposition point, and increasing the flow of the carbonyl to the chamber and heated substrate to continue plating of the substrate without interruption.

9. In a nickel plating process wherein gaseous nickel carbonyl is decomposed thermally in contact with a heated ferrous substrate, the steps of heating the ferrous substrate in an inert atmosphere to a temperature of at least 700° F., eliminating the inert atmosphere from the chamber with a flow of hydrogen about the heated substrate

to thereby also remove oxide from the substrate, displacing the hydrogen with a flow of a gas containing about 50 percent by volume of dry ammonia and about 50 percent by volume of carbon monoxide gas, reducing the temperature of the substrate while in an atmosphere of the latter said gas to about 500° F., flash plating the substrate with nickel metal by providing a low concentration of the nickel carbonyl in the atmosphere of the gas containing the ammonia, reducing the temperature of the substrate while plating to about 375°–400° F., and at the latter said temperature range increasing the concentration of the nickel carbonyl to plate the substrate to the desired thickness.

10. In a gas plating process the method of removing adsorbed, occluded plating interferent gases from a substrate to be plated which includes the steps of providing an atmosphere of a gas containing a mixture of dry ammonia gas and a gas selected from the group consisting of carbon monoxide and nitrogen and wherein at least 25% by volume is ammonia gas, said substrate being heated while in said atmsphere to at least the decomposition temperature of the plating gas, and thereafter displacing the ammonia containing gaseous atmosphere with thermally decomposable metal carbonyl plating gas whereby said metal carbonyl is decomposed and metal is deposited on the substrate.

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