Oct. 5, 1954 J. J. LANDER 2,690,980

CARBONYL PROCESS

Original Filed Jan. 18, 1950 3 Sheets-Sheet 1

FIG. 1

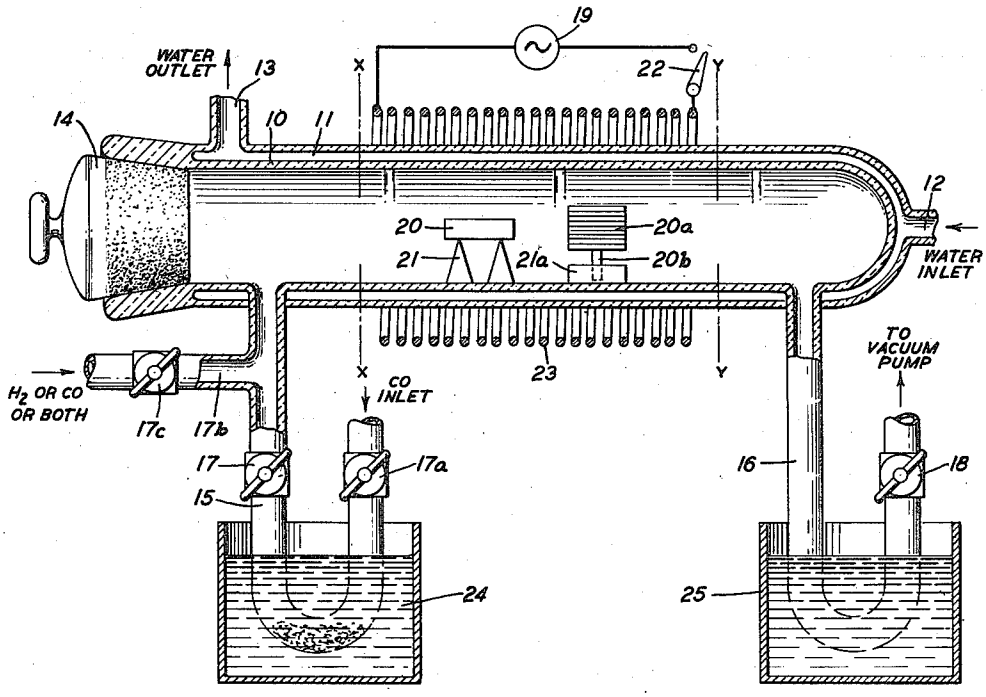


FIG. 1A

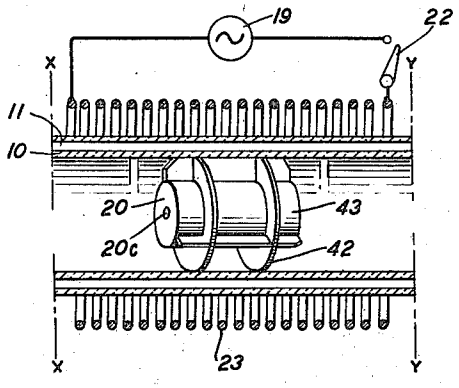
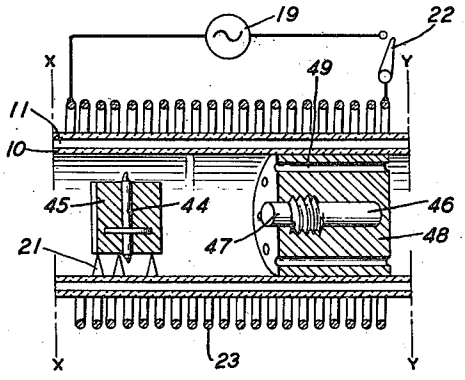


FIG. 1B



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CARBONYL PROCESS

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FIG. 2

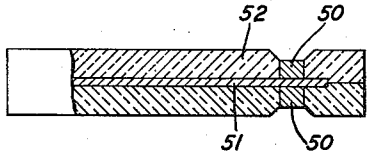


FIG. 3

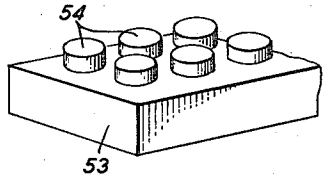
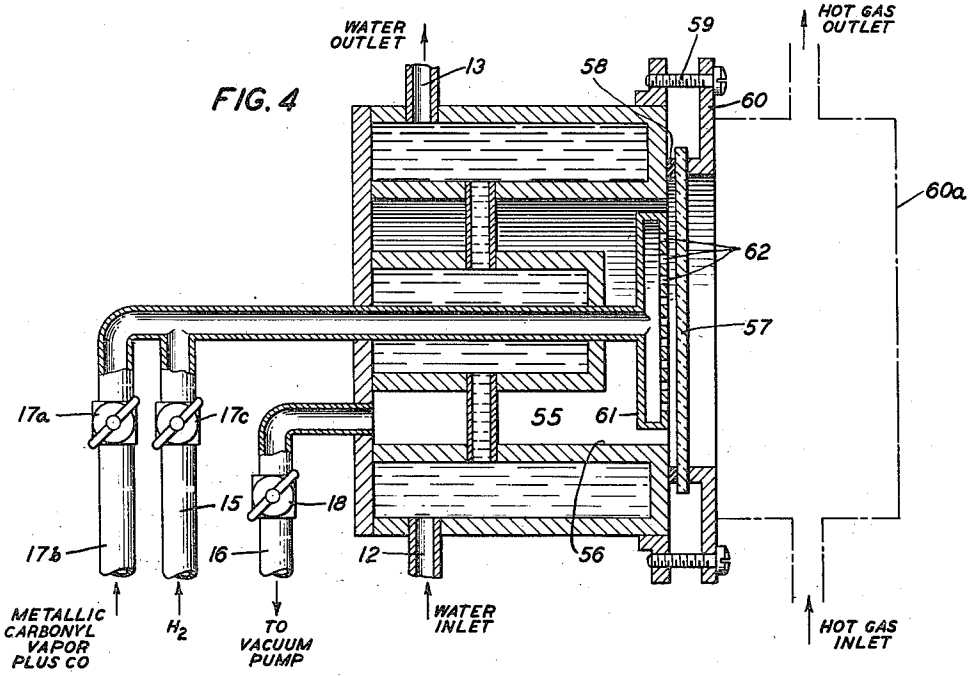


FIG. 4



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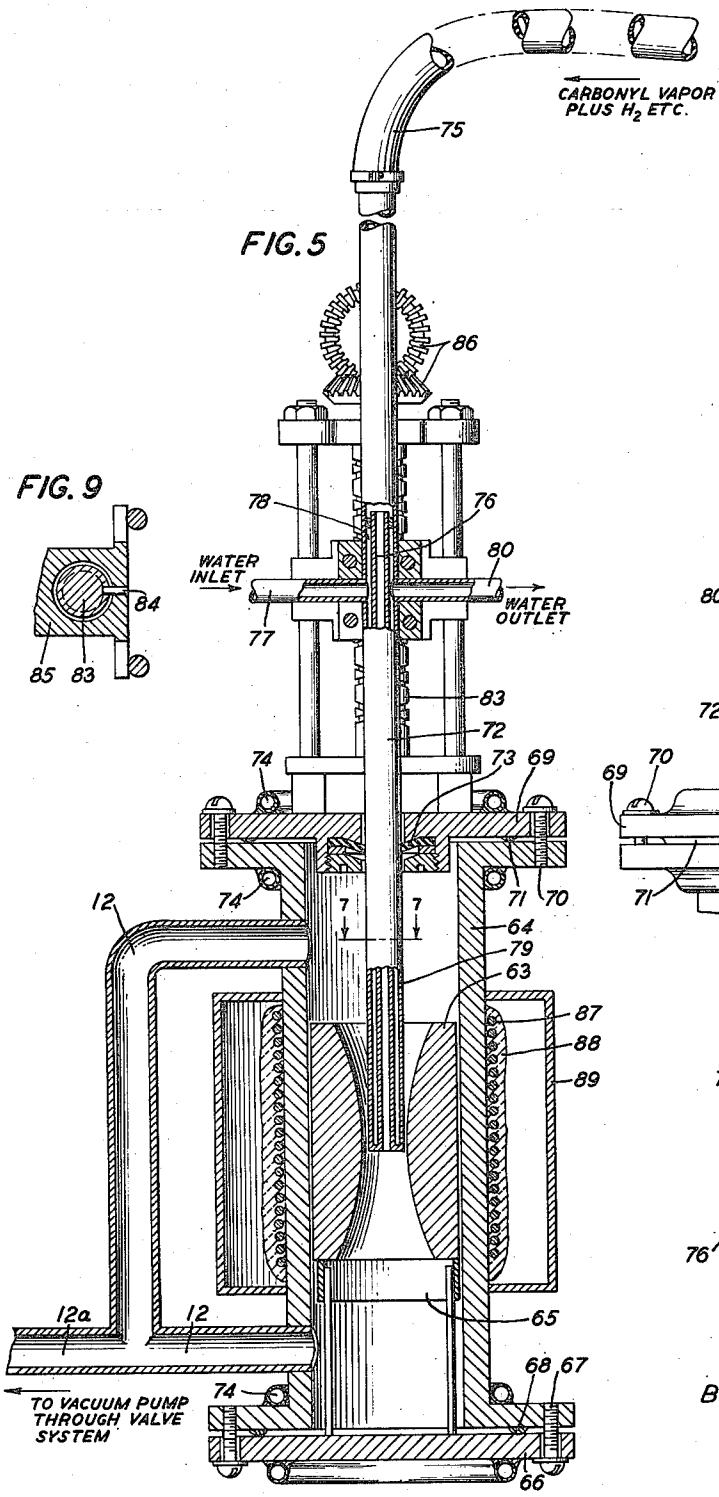

FIG. 5

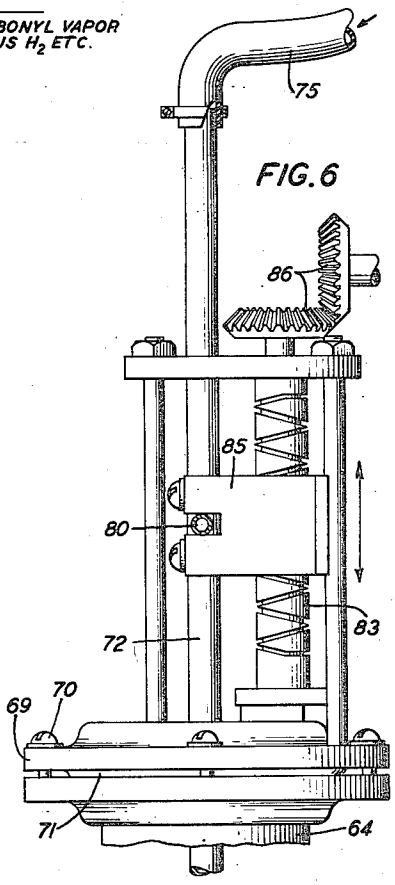

FIG. 6

FIG. 9

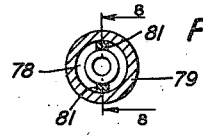

FIG. 7

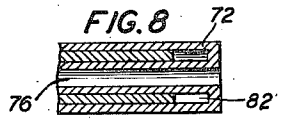

FIG. 8

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UNITED STATES PATENT OFFICE

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CARBONYL PROCESS

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Application January 18, 1950, Serial No. 139,301, which is a continuation of application Serial No. 660,140, April 6, 1946. Divided and this application March 14, 1951, Serial No. 215,522

3 Claims. (Cl. 117—50)

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This invention relates to processes for coating metals such as iron, steel, nickel, copper or other metals and ceramics or vitreous materials, or any other materials capable of withstanding sufficiently high temperatures to be plated with metals or carbides of chromium, tungsten, or molybdenum or compositions including a plurality of such metals or their carbides or mixtures of one or more of such metals or one or more of their carbides.

This application is a division of my application Serial No. 139,301, filed January 18, 1950, which issued as Patent No. 2,602,033 on July 1, 1952, which is a continuation of my application Serial No. 660,140, filed April 6, 1946 which was abandoned March 7, 1950 which in turn is in part a continuation of my applications Serial No. 504,418, filed September 30, 1943, which issued as Patent No. 2,516,058 on July 18, 1950 and Serial No. 525,123, filed March 4, 1944 and abandoned February 19, 1949, and all rights, priorities, and benefits arising from such facts are claimed.

Others have previously suggested the plating of metals with certain other metals deposited from metallic carbonyls under conditions alleged to deposit pure or adhering layers but such suggestions have been defective and insufficient in setting forth the conditions necessary to deposit pure metals or adherent layers and also have failed to recognize that carbides may be so deposited.

There will herein be set forth conditions which must be observed and features of operation and procedure necessary to effect substantial improvements not disclosed by prior workers in the art.

The metals, tungstein, molybdenum or chromium, may apparently exist in different crystalline forms and they also may form several carbides. In accordance with features of the present invention, the processes described may be controlled to deposit platings of the metals in different crystalline forms and may also be controlled to plate carbides in different crystalline forms.

In particular, tungsten and molybdenum may exist in the form of carbides having a hexagonal crystalline structure and a cubic crystalline structure. Conditions may be controlled so that one or the other of these forms of the material may be deposited in the plating.

For certain purposes it may be desired to plate or cover the surfaces of metals or similar objects with coatings, especially tightly adhering coatings of one or another of such carbides or mixed carbides of these metals, or of the metals themselves. For example, an electrical contact

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may be plated with tungsten carbide to produce a durable and arc resistant surface. Also, for example, an electrode or grid may be plated with a form of molybdenum carbide consisting essentially of Mo_2C to make it heat resistant but poorly emissive of electrons or with tungsten carbide consisting essentially of W_2C to make it a good emitter of electrons when heated or Mo_2C or W_2C may be plated to form a hard facing on the object. Among such objects to be plated within the scope of the invention are included space discharge filaments, grids, anodes, electrical contacts, metal cutting tools having their working faces plated, metal working rolls having their working faces plated, metals to be subjected to corrosive gases at high pressures or high temperatures, or both, either or not coincident with mechanical impact, wire drawing dies, bearings, such as clock, watch or compass bearings, mirrors for any purpose such as reflectors of atronomical telescopic instruments.

A feature of the invention relates to the stabilizing effect of carbon monoxide under different conditions of temperature and pressure upon control of the production of definite carbides or relative portions of metals and carbides.

Another feature relates to the avoidance of the detrimental effect of impurities.

Another feature relates to preventing the existence of conditions inhibiting the formation of pure metals or conditions inhibiting the formation of carbides in general, or conditions inhibiting the production of particular carbides and promoting the production and deposition of the particular metal carbide or alloy which is to be deposited.

The invention may be applied to the plating of objects which have internal surfaces, undercut surfaces, depressions or grooves or irregular surfaces with simple or mixed metals, carbides or alloys of the class mentioned, a matter of importance because it is often difficult to deposit material uniformly by plating upon internal surfaces, recesses, or in the bottoms of grooves of objects.

A feature of the disclosure relates to the removal of foreign bodies such as metallic oxides from the surface to be plated to such an extent that foreign bodies of natures and in such small quantities as one might think inconsequential are removed.

Other features of the invention relate to methods of promoting adherence of the plated metals, alloys or carbides to the surfaces to be plated, to the effects of varying one or more of the nature,

pressure, temperature, purity, and kind of gas content supplied to the plating tank chamber, methods of and apparatus for causing plating to be applied on desired surfaces only, and control of the crystal structure or atomic arrangement of the applied plating by controlling pressure, temperature and influx of gases supplied coadjuvantly with the gas or vapor.

A special feature of the invention relates to the use of a continuously maintained reduced pressure in the plating chamber. It is accomplished by sufficiently slow introduction of the metallic carbonyl and other gases coincident with a sufficiently rapid and powerful pumping maintained at a very low degree of pressure in the plating chamber. It is believed that this gives the molecules of metallic carbonyl a long, mean free path whereby the effects of thermal dissociation may be controlled and pure and more adherent coating produced.

Another feature of the invention relates to the control and rate of deposition by introducing carbon monoxide or hydrogen or one of the other or both of these gases in controlled proportions to control the plated composition.

Another feature of the invention relates to the introduction also with the hydrogen of a limited and properly controlled amount of water vapor which, in the case of plating molybdenum or tungsten on certain kinds of objects, is found to be beneficial. In plating with chromium the use of water vapor is excluded and, furthermore, in plating base metals or materials containing substantial chromium contents the use of water vapor is excluded. Thus, for example, in plating molybdenum or tungsten or their carbides upon a kind of steel known as "Stellite" which, in a typical form includes about 27.5 per cent chromium, the use of water vapor is excluded because the chromium becomes oxidized and results in a poorly adherent plate. However, in plating such objects with molybdenum or tungsten the plating may be initiated and carried through the preliminary stages with the exclusion of water vapor and thereafter water vapor may be introduced either for the purpose of controlling or varying the plated composition or for other reasons. In this case the initial deposit of molybdenum or tungsten or their carbides forms a protective layer over the Stellite or other material, which cannot be exposed to heated water vapor in the plating chamber, so that thereafter the water vapor may be introduced.

Carbonyls of tungsten, molybdenum and chromium are white solids which decompose at temperatures of around 150° C. and they have substantial vapor pressures ranging from 15 to 60 millimeters of mercury at 100° C. When they decompose upon a hot metal or similar surface under properly controlled conditions a film of metal or carbide of the metal of the carbonyl or carbonyls is deposited upon the hot surface.

A difficulty encountered in securing adherent deposits has been found to be due, in part at least, to foreign substances upon the surface. One of the most troublesome foreign substances upon the metal surfaces are undesired metal oxides.

A surface to be plated which is suitably free from oxides and other substances may be and has been produced by abrasion, electro-etching, or other chemical methods with prevention of subsequent contamination. Specifically, the metal object to be plated may be treated with acid and washed free of adherent acid in an organic solvent such as alcohol and thereafter placed in the plating vessel hereinafter referred to and subjected to immediately applied vacuum. This serves to remove the residual alcohol by evaporation.

The object to be plated may be treated preliminarily to the introduction of the carbonyl gas by heating to relatively high temperatures such as 600° C. in a vacuum which is maintained by operating the vacuum pump. This tends to clean the surface.

The object to be plated may thereafter be raised to the desired plating temperature, the carbonyl vapor admitted, and the plating accomplished.

However, hydrogen may be admitted to the plating vessel prior to the plating operation with the result that the surface to be plated may be further or more effectively cleaned, with the result of a more perfectly adhering plate. Hydrogen may be admitted to the plating vessel either immediately or after the object has been subjected to vacuum or heat or both for a period of time. The hydrogen is admitted from a suitable inlet and removed by a vacuum pump through suitable outlet and during the time the object to be plated is exposed to the hydrogen the temperature of the object to be plated may be raised as high as 600° C., more or less, dependent upon the nature of the object and its surface impurities with the result that oxides and other substances upon the surface are more thoroughly removed. Thus, for example, oxides will be reduced and the oxygen will combine with hydrogen to form water and carbides lose their carbon and the carbon thereof is combined with the hydrogen to form hydrocarbons such as CH_4. These hydrocarbons are carried out with the hydrogen and eliminated.

The admission of some hydrogen during the plating operation along with the carbonyl vapor and the carbon monoxide gas may be through either the same inlet which supplies the carbonyl vapor or through a separate inlet. In either case an effect of the hydrogen is to produce an effect analogous to that which in electrolytic plating is sometimes styled "throwing power" which signifies that plating in crevices, grooves or depressions is more effectively accomplished and the metal plate is applied more uniformly over the surface to be plated. The influx of hydrogen for the purpose of plating with carbides is subject to the limitations hereinafter set forth.

The deposition of adherent carbide coatings may be accomplished at relatively low temperatures and moderately low vacua with little or no influx of carbon monoxide gas, as increasingly better vacua are employed the use of proportionately greater amounts of carbon monoxide is desirable. The nature of the carbide deposit is also variable with conditions, thus with little or no carbon monoxide gas, at pressures of a few millimeters of mercury, and at low temperatures molybdenum and tungsten carbonyls form chiefly face-centered Mo_2C or W_2C, whereas with higher pressures, higher temperatures, and greater CO gas concentration, in the case of molybdenum carbonyl, MoC is formed. One may introduce appreciable quantities of hydrocarbons of low molecular weight such as methane CH_4 into the plating vessel in the case of plating carbides, especially after the bond has been formed.

Under certain circumstances plating may be accomplished by the use of metallic carbonyl vapor alone in a pure form. For example, in order to plate an iron surface the plating may be started at a sufficiently high temperature to secure satisfactory bond of adherence and deposit metal from molybdenum, tungsten or

chromium carbonyl gas. In plating molybdenum, for example, at a relatively high plating temperature beginning at about 600° C. and continuing in the range of 400° C. to 500° C., metallic molybdenum is deposited provided the influx of carbonyl gas is maintained sufficiently low and the vacuum is maintained also sufficiently low to hold the carbon monoxide gas, CO, to a low concentration. At a lower plating temperature, for example, 200° C. to 400° C., a carbide plating is deposited which has a face-centered cubic arrangement. The tendency is to deposit the cubic carbide at low temperatures and at high concentrations of carbon monoxide. As the temperature is raised and as the concentration of carbon monoxide is lowered, the tendency is to deposit the pure metal molybdenum. At a high temperature and at a relatively high carbon monoxide pressure, the tendency is to deposit a carbide molybdenum Mo_2C which is hexagonal in form. Similar tendencies are noticeable in the case of plating from tungsten carbonyl vapor except that no plating occurs in the range around 200° C. to 300° C. and so far as has been determinable from X-ray analyses, the hexagonal carbide W_2C has not been produced. However, a cubic carbide of tungsten may be produced. The boundary zone between pure metals and carbides is the combined function of temperature and carbon monoxide pressure. The pressures used may range from about $\frac{1}{1000}$ to 10 or 12 millimeters of mercury. From X-ray analyses supplemented by chemical analyses the coatings or platings described as cubic molybdenum carbide occur roughly with the empirical formula Mo_2C although the carbon content in atomic percent varies over a range from around 25 atomic per cent up to about 35 atomic per cent.

Plating may also be accomplished by introducing purified hydrogen along with the gaseous carbonyl in amounts ranging from moderate to very considerable, for example, up to 1000 molecules of hydrogen per molecule of carbonyl vapor. Heating the surface to be plated in hydrogen is beneficial in reducing surface oxides, and, in some cases, it improves the bond between the plating and the surface to be plated and, in other cases, it appears to be fairly essential to producing a satisfactory bond. When the ratio of hydrogen to carbon monoxide gas in the plating chamber becomes large, the tendency is to remove carbon so that pure metals may be plated at somewhat lower temperatures and higher pressures. In general, in plating chromium there is a greater tendency to deposit both oxides and carbides than in the case of molybdenum and tungsten and in the case of this metal and extremely pure metal free from carbides is not deposited but the plating may be made extremely hard. It appears that metalic tungsten can be plated at considerably higher pressures than in the case of molybdenum and therefore the plating rate in the case of tungsten may be higher.

Under many circumstances platings or coatings containing considerable carbon are more hard and brittle than may be desired for certain purposes and the hardness and brittleness may be reduced by introducing a certain percentage of water vapor along with the hydrogen. For example, percentages of water vapor relative to the hydrogen ranging up to fifteen molar and preferably no higher than ten molar per cent may be utilized in the case of plating certain metals as nickel, iron, copper and numerous forms of steel. Some steels, such as those containing chromium, will be oxidized by water vapor and, consequently, water vapor or so-called wet hydrogen may not be used in plating them, although the plating may be started without water vapor and after a sufficient layer to protect the plated object from the water is deposited, the water vapor may be introduced and the plating continued. Subject to these limitations wet hydrogen may be utilized and is beneficial when it may be desired to prevent the deposition of carbon in the plating. For example, in plating molybdenum at 625° C. in a plating gas containing 2 molar per cent of water, plating was found by analysis to contain 0.15 atomic per cent of carbon with a slow plating rate. However, with a considerable faster plating rate and by using 8 molar per cent of water, the plating contained 1.8 atomic per cent of carbon and with a still higher plating rate and 25 molar per cent of water, the plating contained 7.0 atomic per cent of carbon. Therefore, while water vapor is useful in reducing the carbon content, the carbon content can be kept extremely low only at a relatively low plating rate although these may be somewhat higher than may be used for depositing a similar composition without the use of water.

However, one should not conclude that the introduction of oxygen from the air is equivalent to a small added amount of water because the experimental evidence is to the contrary and the introduction of an amount of air equivalent to one per cent oxygen has been found to result in a very inferior plating.

As stated above the introduction of water results in a softer plating, thus, in plating molybdenum at 500° C. and at certain conditions with no water the Vickers hardness of the plating was 1030; with two per cent water 1000; and with eight per cent water it was 800. In plating at 550° C. under similar conditions with no water the hardness was 920; with two per cent water the hardness was 740; with eight per cent water the hardness was 430. Brittleness is a factor and for certain purposes, such as producing a wear-resistant coating on dies, rolls, or machine tools, hardness is highly desirable, but extreme brittleness is not desirable. For such purposes it appears that the best type of plating will be one containing considerable carbon but no carbide as such because the presence of the carbide makes the coating more brittle without increase of hardness. Similar considerations apply to the production of tungsten plating. For example, platings of tungsten containing considerable carbon plated at 450° C. to 500° C. in dry hydrogen at a rather high pressure may have a hardness measured on the Vickers scale above 2000. In plating chromium only relatively hard coatings ranging from Vickers 1200 to 1600 have been produced.

As previously stated, preliminary cleaning of a metallic specimen by abrasion in absolute alcohol is a satisfactory method of producing a surface to be plated. Also in plating some alloys such as "Stellite" electrochemical polishing can be employed. A preliminary step of introducing hydrogen before the metallic carbonyl vapor is introduced is often beneficial in producing a surface to which the plating will form a good bond. At temperatures of 500° C. to 800° C. wet hydrogen is a good cleaning agent for some substances but at lower temperatures quite often only dry hydrogen may be used. Although al-

loyed steel surfaces can under conditions of high purity of hydrogen and good preliminary abrasion be satisfactorily cleaned at 500° C. in hydrogen containing from two to eight per cent water vapor, a more satisfactory technique is to use only dry hydrogen until the temperature of the specimen rises above 500° C. whereupon the wet hydrogen is introduced and the temperature rises continually to 800° C. In plating copper wet hydrogen has been found to be satisfactory in heating the specimen from room temperature to 800° C. In the case of "Stellite" all water must be vigorously excluded and a very high temperature is required for adequate cleaning. Temperatures up to 1000° C. up to 1100° C. have been used. As a general rule, bonding of the plating to the metal to be plated is more satisfactory if the plating is started at relatively high temperatures. Thus in the case of copper a temperature of around 800° C. is suitable and appears to be beneficial. As previously set forth, a high plating rate is undesirable during the bonding step as colloidal particles consisting largely of carbide tend to be produced. Consequently, good bonds require a low plating rate and, in practice, it has often been found desirable to use a rate one-tenth of that which is used at a later stage of the process.

Substances other than metals may be plated within the limits that the substances must be such as can withstand the required high temperature. Within this limitation glass, vitreous materials and other materials may be plated, it being understood, however, that the considerations for forming a good bond vary with the substance which is to be plated.

Foreign materials such as water, air and organic materials must be guarded against whether present in the carbonyl or whether arising from supports or other elements in the plating chamber or whether introduced through leaks in the evacuated system or from other causes. The introduction of such substances is likely to lead to unsatisfactory or, at best, to unpredictable results.

The process may be employed for the formation of plates consisting of alloys. Thus, for example, an alloy of molybdenum and tungsten may be deposited by utilizing carbonyls in a molecular ratio approximately equal to their vapor pressures. Specimens plated at 600° C. with wet hydrogen and at a moderate plating rate were quite hard and brittle while molybdenum alone plated under similar conditions is soft. By employing separate carbonyl chambers with separate controls alloys of various compositions may be similarly produced.

Apparatus useful or convenient for plating the various bodies is illustrated in the accompanying drawings where:

Fig. 1 is a diagram of essential parts of an apparatus which may be employed for plating objects such as sheets, plates, bars, contacts, electrodes, etc.;

Fig. 1A is a modification of a fragmentary part of Fig. 1 between the section lines X—X and Y—Y modified to illustrate one method of securing a suitably thick layer of plating upon the inner surface of an orifice of a metal body;

Fig. 1B is a further modification of a fragmentary part of Fig. 1 taken between section lines X—X and Y—Y illustrating a method which may be employed for plating portions of metallic objects and in plating other portions thereof to an appreciable extent;

Fig. 2 illustrates the modified method of mounting a relay armature so as to plate the working surfaces of its contacts;

Fig. 3 illustrates a method of mounting metallic discs upon a vitreous body to prevent one surface thereof from being plated appreciably while causing other surfaces to be plated;

Fig. 4 illustrates apparatus suitable for plating one side of a disc or sheet of material illustrated as a vitreous material but which may be metal or other substances;

Fig. 5 is a diagrammatic illustration, partially in cross section of an arrangement employing a moving injector for uniformly plating the interior surface of a body having a cylindrical or approximately cylindrical opening therethrough; and

Figs. 6, 7, 8 and 9 illustrate details of the apparatus of Fig. 5.

Referring to Fig. 1 and its operation, a ceramic or glass vessel 10 is provided with a cooling water jacket 11 having a water inlet 12 from a suitable source of supply and a water outlet 13. The inlet and outlet may be located on any suitable portions of the glass or ceramic vessel. The vessel 10 which is illustrated as tubular in form is provided with a large tightly fitting stopper 14 which may be made gas-tight by means of ground glass surfaces or otherwise and has connected to it two other tubes 15 and 16 which are U-shaped. Tube 15 is provided with valves 17 and 17*a* and a side inlet tube 17*b* with a valve 17*c*. Tube 16 is provided with a valve 18. A winding or coil 23 adapted to be traversed by high frequency current supplied from a suitable high frequency source 19 is hung, mounted or otherwise disposed about the tube 10.

An object 20 of metal to be plated or a group of objects may be placed inside the tube 10 by removing the stopper 14; the specimen 20 may be placed on wedge-shaped supports 21 of glass, mica or ceramic material or otherwise hung, supported or disposed within the vessel 10. In some instances it may be merely sufficient to lay the object 20 or group of objects within the vessel 10. The object 20 or objects 20 may consist of iron, nickel, any type of steel or ferrous, cobaltous or nickelous alloy known to the art, as well as metals or alloys of the metals tungsten, vanadium, titanium, molybdenum, tentalum, copper or stainless steel, tool steel, gun metal, cutlery steel, brass, bronze or any other metal of properties similar to these. It may consist of a metallic object to be plated or coated for artistic reasons, or durability, or to produce a hard surface resistant to abrasion or a surface resistance to chemicals in gaseous or liquid form and may be of any shape which may be heated sufficiently uniformly upon the surface or surfaces to be plated by means of high frequency induction. Carbonyl powder, for example chromium, tungsten or molybdenum carbonyl powder is placed in one of the U-shaped tubes, for example, tube 15, and the tube is maintained cold by being immersed in brine, ice water, solid CO_2 or other suitable medium in a container 24. If valves 17 and 17*a* are closed, the tube 15 need not be cooled. The tube 16 is connected to a vacuum pump and the valve 18 opened to thoroughly exhaust the vessel 10 of air.

An alternative object 20*a* consists of a grid for a vacuum or space discharge tube which has a stem 20*b* by which it may be mounted in the tube for use; for plating the stem 20*b* is mounted

in an opening in a block 21*a* of porcelain or glass; from this diagrammatic indication one is not to infer that grids 20*a* and blocks 20 would be plated at one time or that the high frequency heating field suitable for a block 20 would be suitable for a grid 20*a*; in practice a number of grids might be mounted in a multiple block 21*a* and plated at one operation. The grids could be of flat mesh, cylindrical mesh or other desired shape and spacially positioned in the heating field as desired or as necessitated by their respective conformations.

As a preliminary operation, after inserting the object 20 and closing the vessel 10, the carbonyl may be purified by placing it in either tube 15 or 16, exhausting the vessel 10, warming the tube in which the carbonyl is placed, chilling the other tube with solid CO_2 mixture and passing in pure hydrogen over the carbonyl to distill the metallic carbonyl from one tube to the other; gaseous impurities such as H_2O vapor may thus be reduced or eliminated with the hydrogen. This operation may be repeated one or more times or its equivalent may be performed in a separate vessel before placing the carbonyl powder in the apparatus illustrated. The advantage of doing it in the same apparatus lies in the certainty with which recontamination of the material is prevented. We may assume that this step has been performed, if necessary and the carbonyl is in the tube 16 at the beginning of the plating operation.

After the exhaustion or during the exhaustion of the vessel 10 hydrogen may be admitted through tube 15 or 16, preferably in a slow stream through tube 15 until substantially the entire gas content of the tube consists of hydrogen whereupon the switch 22 is closed and the specimen 20 heated to redness by high frequency induction with energy supplied from the coil 23. The hydrogen is then thoroughly exhausted by continuing the operation of the vacuum pump with the valves 17*a*, 17*b*, and 17*c* tightly closed. This tends to remove final traces of impurities. During all this time the carbonyl powder in tube 15 is kept cool by the ice water bath. The specimen 20 is now allowed to cool to a suitable plating temperature, for example around 450° C. The plating temperature may approach 150° C. and the upper limit may apparently approach near the melting point of the metal to be plated. The specimen has been cleaned and all oxides, or substantially all oxides, grease, film, etc. have been removed from its surface by the heating to redness in the presence of hydrogen gas. The vessel 24 is now replaced with another vessel containing warm water at a temperature of about 20° C. and the water in the water jacket 11 is meantime held at around 20° C. The operation of the vacuum pump at the outlet of tube 16 is continued and at this stage or before, if desired, a vessel 25 filled with ice water may be placed around the tube 16. The carbonyl powder in the tube 15 is now vaporized and passes through the tube 10 with the result that there is deposited upon the surface of the specimen 20 a coating of carbides of tungsten, molybdenum or chromium, as the case may be, of a thickness of about 2 mils in approximately 30 minutes. Rapid deposition of the coating is desirable and continuous pumping at the outlet of tube 16 is necessary to remove the carbon monoxide which is formed. The tube 16, being immersed in ice water or other low temperature medium, such as solid CO_2, serves as a trap to precipitate and recover any unreacted carbonyl. After the deposit on the object 20 has reached the proper dimension as may be determined by observation or experiment, the interior of the vessel 10 may be restored to atmospheric pressure, the stopper 14 removed, and the object 20 becomes accessible for removal from the vessel.

In a particular case 0.32 cubic centimeter per second of H_2 was passed over molybdenum carbonyl maintained at 16° C. for 60 minutes at a plating temperature of 370° C. to produce a plate thickness of 0.0022 inch which contained 25.0 atomic per cent carbon and was estimated to consist of 95 per cent molybdenum, or Mo_2C, in gamma or face centered form plus 5 per cent alpha molybdenum. By reducing the plating temperature to 330° C. the carbon was 25.5 atomic per cent and the molybdenum 100 per cent in gamma form. The structure was determined by X-ray examination, the carbon content by analysis.

As an alternative and for some purposes preferred method, the ingress of carbon monoxide either with or without hydrogen along with the metal carbonyl may be continued during the entire plating process and these gases may be caused to enter through the inlet tube containing the carbonyl powder or through another tube. The amount of carbon monoxide used may vary in accordance with the principles elsewhere herein stated. Also when hydrogen or other gases is or are introduced, this may be through the same or a different inlet and for this purpose the apparatus may be provided with as many inlets like 17*b* as desired.

The apparatus of Fig. 1 thus may be employed to produce coatings of tungsten carbide (W_2C), molybdenum or chromium carbides on metallic objects, such as the object 20 or similar objects such as contacts, filaments or other electrodes, edges of cutting tools or other objects. For example, a nickel grid 20*a* for a vacuum tube could be mounted in a ceramic block 21*a* and coated with Mo_2C or W_2C by this method, or a filament could be coated with W_2C.

Fig. 1A represents a modification of Fig. 1 as applied to coat or plate the interior surface of a tubular object with little or no plating of the outer surface. The tubular object 20 to be plated is traversed by a passage 20*c*. It is mounted in a frame of mica which comprises two baffles 42 which substantially fill the cross section of tube 10 and cause all the carbonyl gas to pass through the passage 20*c*. The outer surface is covered with a mica layer 43; the ends of object 20 are in this case left exposed and are plated. Very little deposit occurs upon the surface of the mica and that only upon the part which lies close to the object 20 and thus becomes heated.

In Fig. 1B which is a modification in part of Fig. 1 between the lines X—X and Y—Y, two other objects are illustrated in the plating chamber 10. Ordinarily, however, at most only one class of object would be placed in the plating chamber at a time. These would not necessarily be placed in the positions shown. The principal object of Fig. 1B is to illustrate methods of plating portions of the surface of an object to the exclusion of other portions. A clock pinion mounted on axle 44 may be arranged to be plated on a conical end of the axle. A plastic or vitreous body 45 is made in two or more halves into which the axle 44 and its associated wheel, for example, the balance wheel or pinion, is to be fitted. The

body 45 is mounted on standards or conical supports 21. When the hydrogen is applied the axle 44 becomes heated but the vitreous body 45 does not become heated therefrom for a long time especially as the constant flow of gas including hydrogen carries away the heat fairly rapidly. The plating thus occurs solely upon the conical ends of the axle 45 for the purpose of forming hard bearing surfaces. Platings of tungsten high in interstitial carbide or tungsten carbide may be used for this purpose and platings have been deposited which, on test, were found to be harder than sapphire.

The body 46 may comprise a cylindrical element having a screw threaded portion such as might be utilized for an electrical relay or switch contact to be plated only on its end 47. A plastic or vitreous body 48 may be constructed in two halves and the object 47 placed between the two halves so as to expose only the end 47 which is the only portion to be plated. In the particular arrangement a series of openings 49 are provided to permit the flow of gases through the plating chamber to the outlet 16. In other arrangements the body 46 might not fill the entirety of the cylindrical space in the plating chamber and the openings 49 would be unnecessary.

Fig. 2 illustrates another arrangement of plating the contact surface 50 of a relay armature 51. This armature may be placed between the two halves of a vitreous body 52 so that only the contact surfaces 50 are exposed. The assembly 51, 52 is then placed in the plating chamber in a manner to expose the contact surfaces 50 symmetrically to the stream of carbonyl gas.

Fig. 3 illustrates another arrangement in which a plastic or vitreous body 53 which may consist of glass or porcelain has a number of contact buttons placed upon it so that the upper surfaces and the cylindrical surfaces of the buttons 54 may be plated. The bottom surface resting on the body 53 is substantially unplated and could be welded, or soldered to an armature or other metallic support to serve as an electrical contact.

Fig. 4 illustrates another arrangement in which metallic carbonyls along the carbon monoxide and hydrogen are introduced through pipes 15 and 17b controlled by valves 17a and 17c to the interior of a plating chamber 55. Plating chamber 55 has an outlet tube 16 leading to a sufficiently powerful vacuum pump and controlled, if desired, by a valve 18. A water jacket having an inlet tube 12 and an outlet tube 13 surrounds the chamber 55 whose walls 56 are kept cool. A sheet of material 57 to be plated is placed against the end of the chamber 55 and sealed thereto by rubber or copper gaskets 58 and screws 59 which pass through the flanges of a ring 60 and hold the sheet 57 in a firm, gas-tight manner against the arm of the plating chamber. A chamber 60A conventionally illustrates a flue which may be supplied with hot gases from a furnace to heat the sheet 57 to a desired considerably high temperature during the plating operation. Any suitable source of hot gases or appropriate heating means may be employed. The inlet tubes 15 and 17b are connected to a plating head 61 which is provided on the side towards the sheet 57 with a considerable number of uniform openings 62 through which the plating gases pass to impinge upon the surface of the plate 57. Sheet 57 may consist of glass, vitreous material, any plastic which will withstand the necessary high temperature, and possesses a sufficiently low vapor pressure thereat, or metal sheet of any of the kinds previously enumerated. Sheet 57 need not necessarily be plane but may be curved, be concave or convex or otherwise curved or shaped and the adjacent surface of the plating head 62 may be appropriately shaped in conformity therewith.

Figs. 5 to 9, inclusive, illustrate certain details of an arrangement for plating or coating the interior surface of hollow bodies such as the body 63 which may be long or short and whose interior surface may be straight or curved, grooved or slotted. The body 63 is placed in a cylindrical plating chamber 64 mounted upon a suitable support 65 which is placed in the plating chamber to hold the body 63 in appropriate position. The bottom of the plating chamber is closed by means of a bottom plate 66 held in position by screws 67 and sealed with a copper or other suitable gasket 68. The top of the plating chamber is sealed with a plate 69 held in place by screws 70 also sealed with an appropriate gasket 71. Through an opening in the top plate 69 there extends a hollow moving injector 72 for supplying plating gas to the interior bore of the object 63. The moving injector passes through a gas-tight seal 73 which is more or less conventionally illustrated and may consist of several seals in series. The top and bottom plates 66 and 69 are provided with copper tubes 74 for supplying cooling water during the plating operation. These tubes 74 may be soldered, brazed, or otherwise attached to the end plates 66 and 69 as well as to the upper and lower flanges of the main body 64 for the plating chamber so as to conduct heat away therefrom in an efficient manner.

A flexible hose 75 is firmly attached in an air-tight manner to the upper end of the moving injector 72 for supplying carbonyl vapor along with hydrogen, carbon monoxide and water vapor, if desired, from suitable sources connected by appropriate piping systems and individually controlled by valves. The moving injector 72 has a bore 76 through which the plating gases pass to the interior of the plating vessel 64. The moving injector is also kept cool by means of cooling fluid supplied from inlet tube 77 which passes down a tube or passageway 78 on one side of the center tube 66 and back up through another tube 79 to the outlet 80. The inlet and outlet tubes 77 and 80 may be connected by suitable hose connections to an appropriate supply source and disposal source of cooling water or to a radiator. The bottom end of the moving injector 72 is shown in horizontal cross-section in Fig. 7 and in vertical cross-section in Fig. 8. A septum 81 extending across the tubes separates the passageways 78 and 79 and this septum is discontinuous at the bottom so that the passageways 78 and 79 are connected together by an annular opening 82.

When the plating operation is started the moving injector 72 is traversed upwardly and downwardly by means of a reversing screw 83 which has its groove engaged by a pin 84 (Fig. 9) fixedly engaged in a nut 85. When the reversing screw is driven by suitable gears, such as the beveled gears 86, the moving injector is caused to be moved reciprocally upward and downward so that the end moves from the approximate top to the approximate bottom of the element 63 to supply plating gas to cause a uniform plating along the bore of the element 63.

The element 63 may conveniently be heated by conduction through and radiation from the walls of chamber 64 during plating operation by

a heating winding 87 which may be insulated with asbestos or other heat-resistant material and packed in asbestos packing 88 which may largely or wholly fill the casing 89 which serves further to reduce the radiation and loss of heat to the surrounding atmosphere. The heating element 88 is conveniently supplied with heating current from any desired alternating current or direct current source.

Outlet tubes 12 are connected to a main outlet tube 12a which in turn is connected to a suitable vacuum pump or vacuum pump system through valves as may be desired.

The operation of the arrangement of Figs. 5 to 9, inclusive, will now be briefly outlined. An object 63 to be plated is placed in the plating chamber upon the support 65 by removing the bottom plate 66 and then sealing it back to form a gas-tight connection. The heating winding 87 is then energized and as soon as the object 63 is appropriately hot, pure hydrogen gas may be introduced through the tube 75 and the traversing screw started into operation in order to clean the interior of the object 63 by removing foreign substances and reducing metallic oxides on the surface. After the cleaning has continued for sufficient time, carbonyl vapor, with or without other gases, may be introduced through the tube 75 and the plating operation is commenced. Initially the object 63 is maintained at an appropriate temperature to form an effective bond of the plating on the surface to be plated and thereafter the temperature of the object 63 may be regulated by increasing or decreasing it to a temperature appropriate to the desired speed of plating and the amount of carbonyl vapor, hydrogen, carbon monoxide, with or without other gases, such as water vapor, which may be introduced. At the end of the operation the carbonyl gas is cut off, the object 63 is allowed to cool and it may then be removed from the plating chamber whereupon the apparatus is in condition for repeating the operation to plate another object.

The arrangements described are exemplary for indicating various types of arrangements which may be employed for plating the whole or parts of surfaces and the parts being of various sizes and shapes.

Tungsten carbide having the formula W_2C, with a small variable excess or one or the other of carbon or tungsten, may be plated; this plating is very hard. This hardness is considered to arise in part from the smallness of the crystals in the plate. Note is also made of the fact that the plating is free from iron, nickel, cobalt, or similar elements. Likewise, adherent plating of Mo_4C and Mo_2C or mixtures thereof which are hard can be produced.

Tests of carbides of composition Mo_2C and Mo_4C and upon platings consisting of various proportions of those carbides with molybdenum show that many of these platings have unexpected hardness. They are often composed of fine crystals and under some conditions which may be experimentally determined by X-ray analysis, the crystals have a strong orientation. As previously set forth, pure metals and alloys may also be deposited. In practice the last vestige of carbon cannot be eliminated from the plated metal although under appropriate conditions the carbon content may be made quite small or so small as to be insignificant in affecting the properties of the product.

The hardness combined with toughness in varying degrees together with resistance to corrosion makes the process available for the production of various useful products, such as plated or coated working surfaces for wire drawing dies, cutting tools, machine drills, rolls, engine bearings, valves of internal combustion engines, taps, reamers, metal slitting saws, pinion bearings, nozzles, and rotors and stators of high temperature turbines, as well as the blades of combustion chambers of internal combustion turbines which may be rendered less subject to corrosion by plating with suitable carbides of chromium, tungsten or molybdenum or by a mixture thereof with metals.

Rolls of cylindrical or rolling pin form may be supported at the centers of their ends by ceramic supporting frames including a ceramic holding screw in a manner similar to the method of holding a work piece in a lathe. Similar or analogous methods may be employed to plate the whole or working surface of valves such as the valves of internal combustion engines. The whole or the working faces of precision tools, such as guages and guage blocks which are required to be hard and of exact dimensions, may also be plated by one or more carbides or by mixed carbides.

A metal coated with an adherent layer as defined herein signifies a condition of powerful adherence whereby the metallic body may be stretched or distorted or subjected to high temperatures or high pressures or both without separating the layer. In the case of tough layers of plated material, this stretching or distortion without cracking or breaking may be considerable; when the plated layer is hard and brittle the stretching or distortion may be slight before cracking or breaking, not because the adherence is less but because the plated metal will crack or break upon stretching or distortion but will nevertheless tend to adhere strongly even though cracked. A mere superficial attachment is not considered to be adherence in the sense of this specification.

What is claimed is:

1. The method of plating a surface which comprises maintaining the surface to be plated at a temperature of from 200° C. to 600° C., passing carbonyl vapor of a metal selected from the group consisting of tungsten, chromium and molybdenum together with carbon monoxide in addition to that produced by decomposition of carbonyl and up to 1,000 molecules of hydrogen per molecule of metallic carbonyl over the surface to be plated, and maintaining the pressure at from 0.001 to 12 millimeters of mercury at the surface.

2. The method of claim 1 in which the surface to be plated is maintained at a temperature of from 500° C. to 600° C. and in which the carbonyl is molybdenum carbonyl.

3. The method of claim 1 in which the surface to be plated is maintained at a temperature of from 450° C. to 500° C. and in which the carbonyl is tungsten carbonyl.

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