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CHROMIUM NICKEL ALLOY GAS PLATING

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FIG-1

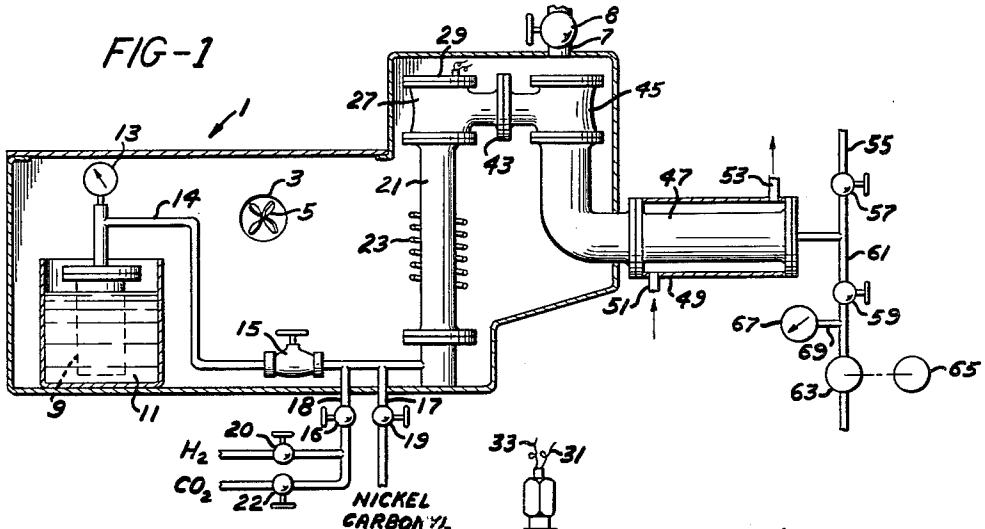
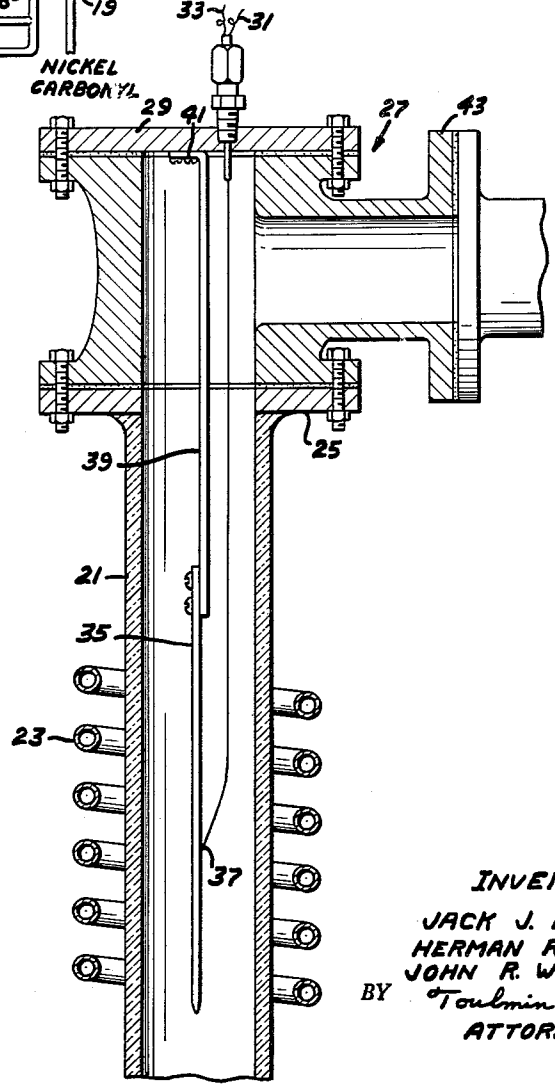


FIG-2



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CHROMIUM NICKEL ALLOY GAS PLATING

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This invention relates to alloys and alloy coatings and to processes and apparatus for attaining the alloys; more specifically the invention relates to the formation of coatings of chromium and nickel by the simultaneous deposition of the metals from thermally unstable compounds of chromium and nickel.

This application is related to copending applications of Nack et al., Serial No. 316,695, filed October 24, 1952, now Patent No. 2,767,464, and Serial No. 374,398, filed August 14, 1953, now Patent No. 2,898,234, both assigned to the same assignee as the present invention.

It is a primary object of this invention to provide a novel method for the attaining of reproducible chromium-nickel alloys.

It is an important object of this invention to describe a novel two temperature process for the production of alloys.

It is a principal object of the invention to describe a novel process for the production of alloy coatings on bases in which one of the metals constituting the alloy is initially plated on the base prior to alloy deposition.

It is yet another object of the invention to describe an alloy plating process using thermally decomposable metal bearing gases, in which process the temperature of the material to be plated is, from the initiation of the plating to the termination, always above the temperature of decomposition of one of the gases and after the initiation of the plating is raised to the decomposition temperature of another of the gases.

It is still another object of this invention to describe novel apparatus useful in the plating of alloys from heat decomposable compounds having widely different vaporizing characteristics.

The invention particularly contemplates the deposition of alloys of chromium and nickel on metal bases such as copper, iron, nickel, steel and other alloys, as well as on non-metallic material capable of withstanding the temperature to which the bases are necessarily exposed in the process of invention.

The invention further contemplates a process in which the plating gases are supplied to the piece to be plated in voluminous quantities such that decomposition products of the plating gas are quickly diluted by undecomposed gas and are hindered from contacting the plated metal. No inert carrier gas is employed and relatively large quantities of the plating gas are recovered undecomposed.

Essentially in the process of invention high flow rates of heat decomposable gases are maintained, the gases of the flow being effective to dilute readily the gases of decomposition and to inhibit the contact thereof with the surface being plated. Carbide formation is thus inhibited and substantially pure coats are attained.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:

FIGURE 1 schematically illustrates the apparatus arrangement of invention; and

FIGURE 2 is a view illustrating a preferred arrangement for supporting the base material within the apparatus.

Referring to FIGURE 1 there is indicated generally at 1 a housing having an opening 3 in which a fan 5 is

positioned for supplying heated air to the interior of the housing. The upper portion of the housing is provided with an outlet portion 7 having a valve 8 for control of the flow of heated air through the outlet.

Positioned within the housing 1 is a vaporizing chamber constituting substantially a steel tubular member 9 closed at one end and supported within a constant temperature bath 11 as of oil heated by means (not shown) to a temperature of 200° F.; the chamber contains solid chromium hexacarbonyl which vaporizes under the influence of the temperature applied.

A gauge 13 is positioned in a conduit 14 for measuring pressures occasioned by the flow of chromium hexacarbonyl vapors to a valve 15 when the latter is open. A conduit 17 extends through the housing 1 and is provided externally thereof with a valve 19 leading to a source of supply of nickel carbonyl vapors, which source is maintained at about room temperature. Extending also through the housing 1 is a conduit provided externally of the housing with a valve 16 for controlling the selected flow of either hydrogen or carbon dioxide from sources generally indicated by legends. Opening of valve 20 and valve 16 permits the flow of hydrogen into the system with valve 22 closed, while opening of valve 22 and valve 16 permits the flow of carbon dioxide to the system. The sources of supply for these gases may be arranged in any convenient manner, but should be externally of the housing 1.

A Pyrex plating chamber 21 which is itself surrounded by an induction heating coil 23 is connected to the valves 15 and 16 by suitable conduits. As shown more clearly in FIGURE 2 the Pyrex heating chamber is secured to the lower end of a T connection 27 having an upper plate 29 which closes the upper end of the T and is suitably secured thereto in gas-tight relation by a nut, bolt and compressed gasket arrangement.

Leads 31, 33 of a thermocouple are air tightly secured through the upper plate 29 and pass downwardly to contact a metal workpiece 35 which is to be plated with the alloy coating; the leads are suitably secured to the workpiece as at 37.

The workpiece 35 is of copper and is itself supported by a rod 39 secured to the upper plate 29 in any convenient manner as by nuts and bolts indicated at 41. The arm 43 of the tee extends rightwardly in FIGURE 1 and is connected to the tee 45 for the passage of gases to a condenser 47 which is itself surrounded by a water jacket 49 having an inlet port 51 and an outlet port 53. Condenser 47 serves to condense out undecomposed gases of hexacarbonyl and the condenser is for this purpose positioned on the outer side of the housing 1 as shown. Secured to the right hand end of the condenser 47 is an exhaust conduit 55 having a valve 57 which valve is normally closed in the operation of the apparatus. Valve 59 is provided in conduit 61 the remote end of which is provided with a vacuum pump 63 and a motor 65 to provide vacuum pressures on the whole system. Branch line 69 is provided with a manometer 67 for the measurement of pressures in the conduit 61.

In the operation of the apparatus sample 35 to be plated is suitably suspended from the plate 29 which is then secured to the tee as shown in FIGURE 2 and at the same time the thermocouple leads, which have been secured to the sample, are also inserted into the system (FIGURE 2); the motor 65 and vacuum pump 63 are then operated with valve 59 open and valve 57 closed, valves 15, 16 and 19 also being closed, to evacuate the system.

Preferably at this time the hot air bath of the system has a temperature of about 200° F. and this assists the clearing of the system of all gases. When the pressure has been reduced to a low point valves 16 and 22 are

preferably opened to permit carbon dioxide to be drawn through the system to insure of complete evacuation of the air therefrom. The presence of even small amounts of air may tend to form nitrides which are desirably avoided.

During the flushing of the system induction heater **23** is also operated in order that the workpiece **35** may itself be subjected to high temperatures to drive therefrom any gases possibly included within the sample. With the system thus freed of gases and valve **22** closed hydrogen is lead into the system by opening of valve **20** and the temperature of the workpiece is at this time raised to about 1000° F. A sufficient flow of hydrogen is first attained to completely fill the system and valve **20** is then shut off and the system pumped down to insure of complete removal of all gases other than hydrogen. Valve **20** is then again opened and a moderate flow of hydrogen is maintained through the system with the workpiece **35** at a temperature of about 1000° F. to reduce any oxide layer which may have formed on the copper workpiece subsequent to the usual sanding and degreasing operation in preparation of the workpiece for plating.

Valve **20** is then closed and the system evacuated, whereafter valve **19** is opened to permit a flow of nickel carbonyl into the system at a rate sufficient to maintain the system pressure, as measured by the manometer **67**, at between about 0.02 to 0.2 millimeter of mercury. The nickel carbonyl which decomposes at a relatively low temperature upon contacting the highly heated workpiece flashes a coating of nickel thereover and the flow of nickel carbonyl is maintained in this instance for a sufficient length of time to provide a nickel coating on the copper of about 0.2 mil.

In the practice of the invention it is customary to continue the plating process without removal of the sample from the chamber but when such a sample is removed for inspection of the plating at this stage it is found that the nickel deposit is bright, smooth, adherent to the copper base, and substantially free of carbon. Normally of course such sample is not removed at this stage, but with nickel carbonyl still flowing into the system the temperature is reduced in the nickel carbonyl atmosphere to about 350° F. which temperature is below that of the decomposition of chromium carbonyl.

It is to be noted in this latter respect that chromium hexacarbonyl is most difficult to obtain, being most expensive, and when obtained may contain impurities which materially alter its characteristics. In the present case the chromium carbonyl sample was pure and at 350° F. substantially no decomposition took place when the chromium carbonyl was introduced into the system.

As the chromium carbonyl is introduced by the opening of valve **15**, a pressure of the hexacarbonyl having developed due to the immersion of chamber **9** in the oil bath **11**, the nickel carbonyl flow is also materially increased; if desired the nickel carbonyl flow may first be increased to the desired extent and then the chromium hexacarbonyl may be mixed with the nickel carbonyl flow; this permits of measuring directly the pressure occasioned by the nickel carbonyl and the pressure due to chromium hexacarbonyl is attainable by difference. With a vapor pressure of chromium carbonyl and nickel carbonyl in the system of about 2 mm. of Hg, and with the hexacarbonyl in material excess, the temperature is raised to about 390° F., at which both the chromium and nickel plate out together. This plating condition is held for a period of about 10 minutes and the thickness of the deposit attained is about 1.25 mil on each side of the flat copper bar. The temperature of the piece to be plated should not exceed 425° F. in order to maintain carbide formation low.

It is to be noted that at any given partial pressure of the chromium hexacarbonyl the amount plated in a given time increases materially and with temperatures between 370° F. and 425° F., while for nickel carbonyl at a given partial pressure the amount plated is very nearly constant over a temperature range of 350°–425° F.—consequently changing the chromium hexacarbonyl flow is best adapted to change the nature of the plate.

An analysis of the plated alloy thus attained showed 94% chromium, 5.3% nickel and about 0.7% of carbon. The material was lustrous, hard and highly suitable as a coating material due to its highly adherent nature.

Increasing the pressure of nickel carbonyl increases the percentage of nickel in the resultant alloy; alloys of chromium and nickel varying from 5 to 80% by weight of nickel may be so prepared; a most important alloy being one containing 80% of nickel and 20% chromium by weight.

Maintaining the chromium content of the alloy high appears to improve the smoothness and uniformity of the product and the texture of any of the alloys appears more smooth than either a pure nickel or pure chromium coating.

It is to be noted that the process may be effected with both metallic and non-metallic bases, ferrous bases being very suitable; in some instances non-metallic bases to which the plated alloy does not readily adhere may be employed, and under these circumstances the alloy may be stripped from the base to be used for other purposes.

It is not necessary to the process of invention that an initial deposition of nickel, for example, occur prior to the deposition, for example, of the nickel and chromium alloy, but such is preferable wherein very high adherence to the base is desired.

It has been found most suitable to introduce the mixture of heat decomposable gaseous compounds to the heated base while the base is at a temperature which is below that of the decomposition point of at least one of the compounds. Apparently this contributes to alloy formation; the nickel carbonyl however should be at such low pressure when introduced alone that the gaseous products of decomposition are quickly removed by the pump. In fact the appropriate nickel carbonyl pressure should be determined quickly and the chromium introduced in copious quantities immediately thereafter.

The presence of large volumes of undecomposed carbonyls quickly dilutes the products of decomposition such as CO and materially reduces the tendency toward carbide formation. Such procedure results of course in much undecomposed chromium and nickel carbonyl passing through the system but these may each readily be collected.

In the specific example set out hereinbefore wherein the alloy is high in chromium the nickel is substantially completely decomposed and chromium hexacarbonyl serves as the diluent for the gases of decomposition; accordingly much chromium hexacarbonyl was collected at **47** in this plating operation. It is to be noted that the pound price of chromium hexacarbonyl is presently exceedingly high and recovery is substantially a pre-requisite to such operation.

Carbon is found in the alloy only in very slight amounts. This is in direct contrast to prior art chromium metal depositions where customarily the carbon is present to the extent of about 5% by weight. No oxygen or nitrogen whatsoever was found in samples produced in the method of invention.

This high degree of purity is attributed to the diluent effect of the plating gases present in high volume, and the absence of carrier gas is also of assistance in this respect, and particularly important is the exclusion of hydrogen though this is not the most material factor in the invention.

It may be noted that the practice of invention may be modified by first plating a nickel film at a temperature which is above that of the decomposition point of the particular nickel bearing employed but below that of the decomposition point of the chromium. Thus it is not necessary to raise the temperature excessively and to

cool in the nickel carbonyl atmosphere in order to practice the invention. However, it has been found that cooling in the nickel carbonyl atmosphere contributes to uniformity and smoothness of plate.

Other compounds may be employed for chromium deposition and for nickel deposition in the practice of the invention and other metals may be formed into an alloy, for example, nickel and molybdenum or chromium and molybdenum, by the process of invention, it being only necessary to adjust particular temperature conditions to accommodate the metal bearing gaseous compounds selected. Further, more than two metals may be plated to form the alloy if such is desired.

In fact, it has been found that in alloy formation to effect control of the plating operation it is primarily necessary to have a large volume of at least one of the gases present to such an extent that a very substantial amount thereof passes through the plating chamber undecomposed, and in general, and in the specific example set out hereinbefore, the volume of undecomposed gases passing from the plating chamber will be greater than that of the gases of decomposition.

Further, the temperature should be maintained as low as is consistent with the thermal decomposition point of the compounds involved. Consequently low pressures are preferred in order to suitably attain both large volumes and low temperatures in an adequate working range. This necessitates a flow rate sufficient to attain the dilution of the gases of decomposition and the flow rate may vary widely with the plating rate desired.

Also, in all instances wherein a high degree of adhesion is desired it is preferred first to plate a coating of metal from that compound which decomposes at the lower temperature and to reduce the temperature of the piece in an atmosphere of that compound. The reduction in temperature takes place preferably to such an extent that the temperature must again be raised in order to effect decomposition of the compound containing the second metal.

The alloys which contain a major proportion of chromium and a minor proportion of nickel are particularly suitable for use in conjunction with electrical components; for example, the alloy coating may form the high resistance conductive material in an electrical resistor, the base on which the alloy is coated being preferably in this circumstance an electrically non-conductive material such as ceramic or glass.

The alloy may also form a coating over a conductive base such as copper as described hereinbefore for use in the anodes of discharge tubes and in X-ray tubes. X-ray diffraction patterns show the formation of a unitary lattice by the metals constituting the alloy. Further, a characteristic property of the alloys in general is highly acid resistance, that is they do not dissolve in H_2SO_4, HCl, or dilute HNO_3.

The effectiveness of the process of invention in producing substantially pure alloy coatings is attributed to the use of high flow rates of the plating gases, sufficient to quickly dilute gases of decomposition (which inhibits the metal-catalyzed formation of carbide from CO) at low temperatures, and preferably at low pressures in the absence of carrier gases. It has been found that at high temperatures of plating carbide formation is induced, carbide formation apparently being further facilitated by the presence of reducing carrier gases such as hydrogen, both high temperature and reducing gases being commonly employed in chromium plating and molybdenum plating in the art.

It will be understood that this invention is susceptible to modification in order to adopt 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.

We claim:

1. In a process of producing a highly adherent alloy coating on a metal base, the steps of providing sources of heat decomposable gaseous metal compounds of the metals which are to constitute the alloy, heating a metal base in an evacuated zone to a temperature which is above the decomposition temperature of each of said gaseous metal compounds, flowing a gaseous stream of one of the gaseous metal compounds over the base to effect the deposition of a thin coating of one metal thereon, reducing the temperature of the base to below that of the effective decomposition point of only that gaseous metal compound which decomposes at the highest temperature, flowing a copious stream of mixed gases of the gaseous metal compounds over the heated base, raising the temperature of the base to the effective decomposition point of the mixture of gaseous metal compound to effect deposition of the metals, and removing the gaseous products of the thermal decomposition with undecomposed gases from the evacuated zone.

2. In a process of producing a chromium-nickel alloy coating on a copper base, the steps of providing sources of gaseous nickel and gaseous chromium carbonyls, heating the copper base in an evacuated zone to a temperature of about 1000° F., flowing a gaseous stream of gaseous nickel carbonyl over the base to effect the deposition while maintaining the temperature at about 1000° F., reducing the temperature of the base in a gaseous nickel carbonyl atmosphere to below that of the effective decomposition point of gaseous chromium carbonyl but not below that of the nickel carbonyl, flowing a copious stream of mixed gases of the chromium and nickel carbonyls over the heated base, and raising the temperature of the base to the effective decomposition point of gaseous chromium hexacarbonyl to deposit chromium and nickel on the base, and removing the gaseous products of the thermal decomposition with undecomposed gases from the evacuated zone.

3. The process of plating a nickel-chromium alloy on a base metal to secure high adherence qualities, the process involving the steps of heating the base metal in an evacuated zone to a temperature of about 1000° F., contacting the base metal while at the said temperature with a light flow of nickel carbonyl gas, reducing the temperature of the base metal while in contact with the nickel carbonyl gas to a temperature which is below the decomposition point of chromium hexacarbonyl, directing a copious flow of the mixed gases of gaseous nickel carbonyl and gaseous chromium hexacarbonyl against the surface of the base metal while the temperature thereof is below the decomposition point of chromium hexacarbonyl, and then raising the temperature of the base metal to between 390–425° F. while in contact with the copious gas flow to effect deposition of an alloy of chromium and nickel on the base metal.

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