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Report No. 8926-088

Materials - Finishes and Coatings - Vapor Deposited
Nickel, Iron, Chromium, Molybdenum -
For Joining Stainless Steel and Titanium Alloy

Plating and Joining Characteristics

F. M. Graber, T. D'Annessa, V. Ianucci

20 January 1959



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Abstract

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Reference: Graber, F. M., D'Anessa, T., Ianucci, V.,
"A Study of the Joining of Metals By The
Decomposition of Some Organometallic Compounds,"
General Dynamics/Convair Report ZR-658-046, San
Diego, California, 20 January 1959. (Reference
attached.)

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A STUDY OF THE JOINING
OF METALS BY THE DECOMPOSITION
OF SOME ORGANOMETALLIC COMPOUNDS

BY

F. M. GRABER, T. D'ANNESSA, V. IANNUCCI

JAN . 20, 1959

ENGINEERING DEPARTMENT

C O N V A I R
A Division of General Dynamics Corporation
(San Diego)

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Title: MATERIALS - FINISHES AND COATINGS - VAPOR DEPOSITED NICKEL, IRON, CHROMIUM, MOLYBDENUM - FOR JOINING STAINLESS STEEL AND TITANIUM ALLOY. PLATING AND JOINING CHARACTERISTICS.

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I. SUMMARY:

A study of the joining of metals (in the form of a tee joint) by the decomposition of organometallic compounds yielded information as to the major problems involved. It appeared that inability to form a fillet and lack of throwing power are major problems. Deposited coatings became thinner near the tee joint, resulting in a joint of low strength and little practical value. Further research and development may overcome these difficulties.

Vapor plating of nickel and iron resulted in a ductile adherent coating on 17-7 PH stainless steel and titanium alloy. Vapor plating of chromium and molybdenum produced adherent coatings which proved to be brittle. Vapor plating should be investigated as a means of producing plated parts without hydrogen embrittlement. Advantage should also be made of coatings made by vapor deposition at high temperatures because these coatings are frequently more adherent, less porous and more stable under high temperature, than coatings applied by other methods at low temperatures.

Experiments on the joining of metals and honeycomb sandwich by electroless nickel and induction resistance welding indicate that these methods may warrant further investigation.

II. INTRODUCTION:

It was proposed by Dr. Critchfield of the Convair Scientific Research Laboratory that reactions of certain organometallic compounds where the pure metal is obtained from the gaseous state might be applied to the production of brazed joints in honeycomb structures.

Certain inherent advantages would be realized if honeycomb structures could be fabricated in this fashion. Joints of pure metals such as nickel, molybdenum, chromium, etc. could be utilized at temperatures higher than the maximum service temperature of the present brazing alloys. Also, the relatively low temperatures necessary for these reactions would be more compatible with the heat treatment of the sandwich materials. The actual bonding of the joints could be performed prior to heat treatment, during various stages of heat treatment, or in the fully heat treated condition, depending upon the desired end characteristics. The latter advantage could greatly reduce the current high cost of fabricating honeycomb structures.

III. OBJECT:

The object of this investigation was to determine if it is feasible to fabricate metal honeycomb sandwich structures using, as the bonding agent, metals obtained from metal organic compounds.

IV. DISCUSSION OF THE LITERATURE:

Metal deposition by decomposition of metallic organic vapors was started in England in 1890 when Mond chanced upon the first vapor deposition phenomenon while studying the effects of finely divided nickel on CO. Interest in vapor deposition temporarily waned. However, from 1909 to 1939, attention was again directed to vapor deposition when various halide-reduction and halide decomposition processes were used to prepare tantalum, titanium, zirconium and other refractory metals. The development of vapor deposition as a means of applying protective coatings took place largely after 1935. ¹

Vapor deposition consists essentially of reducing or decomposing a volatile compound of the coating material upon a heated surface. For the practical employment of this method, the material must form a volatile compound which can be readily disassociated or reduced at temperatures below the melting points of the coatings or of the base material, but which is sufficiently stable to prevent decomposition or reduction before reaching the deposition surface. Coatings made in this way at high temperatures are frequently more adherent, less porous, and more stable under high temperature operation than materials deposited at lower temperatures by other methods. For this reason vapor deposited chromium and nickel coatings are being used increasingly for high temperature applications, although these metals can be more easily applied by conventional deposition. ^{1,2}

IV. DISCUSSION OF THE LITERATURE: (Continued)

Two general methods for vapor deposition are used: ¹

(1) Reduction or displacement

- (a) Hydrogen or metal reduction of halides.
- (b) Reaction of halides with a gas containing carbon, nitrogen, boron, silicon, or oxygen compounds.
- (c) Displacement or reaction of base material with one of the constituents of the gas phase.

(2) Thermal decomposition

- (a) High temperature decomposition of halides and oxygen containing compounds.
- (b) Low temperature pyrolysis of carbonyls, hydrides, arenes, etc.

It was decided to concentrate the literature and experimental work on the decomposition of metallic organic compounds containing iron, nickel, and chromium, as these are the major elements present in 17-7 PH stainless steel which is of interest in metal honeycomb bonding. Molybdenum was also investigated because of its high temperature applications.

Iron:

Iron can be vapor deposited by hydrogen reduction of ferric chloride vapor at 650°C.³, by thermal decomposition of ferrous iodide in vacuo at 1100°C., using a vaporization temperature of 500°C.⁴, or most readily, by the pyrolysis of iron carbonyl. ^{5, 6, 7, 8} The literature ^{5, 6, 7} indicates that iron pentacarbonyl decomposes at temperatures

IV. DISCUSSION OF THE LITERATURE: (Continued)Iron:

as low as 60° to 140°C. The most satisfactory and adherent heavy coatings are obtained at 370° to 450°C. Iron coatings are extremely brittle in the as deposited state, probably because of carbon deposited with the iron. The coatings can be rendered ductile by annealing in hydrogen at 900°C. for 20 to 30 minutes.

Nickel:

Nickel can be deposited in an adherent, ductile form by thermal decomposition of nickel tetracarbonyl at 140° to 240°C. The optimum deposition temperature ranges from 180° to 200°C. 7, 9, 10, 11 Above 205°C. finely divided nickel is formed which catalyzes the disproportionation of carbon monoxide, causing carbon to deposit along with the nickel.

Nickel can also be deposited at 350°C. to 450°C. from nickel acetylacetonate ¹² vaporised at about 160°C., preferably at reduced pressure.

Chromium:

Chromium can be deposited from its halides ¹, however these compounds are all so non-volatile that the use of fused silica, vycor or metal

IV. DISCUSSION OF THE LITERATURE: (Continued)

Chromium:

equipment is required in both the thermal decomposition (1200° to 1400°C.)^{1, 13} and the hydrogen reduction processes.

(1000° to 1200°C.)^{1, 14 15}

Attempts have been made to vapor deposit chromium at low temperatures by reduction or decomposition of chromyl chloride¹⁶ and by pyrolysis of chromium carbonyl.^{17, 18, 19} Lander and Germer¹⁸ experimented briefly and not too successfully with the chromium carbonyl pyrolysis process. In a more extensive investigation, Owen and Webber¹⁹ obtained deposits of varying chromium content on steel from a mixture of the carbonyl and hydrogen at reduced pressures and a temperature of about 450°C., where the highest purity (95% Cr, 5% Cr₂O₃) deposit was obtained. At 625°C., a deposit of much lower purity (40% Cr, 60% Cr₂O₃ + Cr₃C₂) was obtained. At both these temperatures, well bonded deposits resulted, but at other temperatures (250°C. to 650°C.) the deposits were poorly bonded and contained varying amounts of oxide and carbide.

A technical information bulletin²⁰ from Union Carbide Chemical Co., suggests the use of some of the more recently prepared compounds;

IV. DISCUSSION OF THE LITERATURE: (Continued)

di-benzene chromium, di-toluene chromium, and di-cumene chromium, for vapor plating involving chromium. Some of the novel properties and unique structure details of these arene compounds are discussed in Berichte 21, 22, 23, and Naturforsch. 24, 25

A number of patents, 26 to 41 mostly by The Commonwealth Engineering Company of Ohio, Dayton, Ohio, are listed which refer to vapor phase metal plating using $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$. Commonwealth also states ⁴² that it is possible to plate alloys from mixtures of metal gas compounds. Certain alloys such as stainless steel can be plated from the gas phase. ⁴²

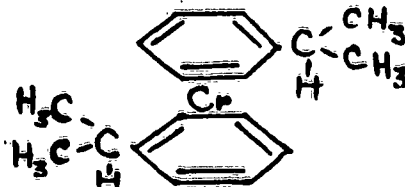
In all the references mentioned so far no mention is made of bonding two metal substrats, by vapor deposition; only vapor phase plating is discussed. The only reference which mentions the use of this technique for bonding was found in a patent ⁴³ given to P. Pawlyk et al. of Commonwealth Engineering Company. This patent describes the use of nickel carbonyl and nickel acetylacetonate in the formation of metal-to-metal seals which are composed of finely deposited metal for the purpose of preventing leakage into evacuated containers such as electron tubes. No details are given about the strength of the bonds.

V. MATERIALS:

The following compounds were used in this experimental study:

- (1) Molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$ v.p. at $55^\circ\text{C}.$ $\sim 2.3\text{mm}.$; obtained from Climax Molybdenum Company, 500 Fifth Avenue, New York 36, New York.

- (2) Di-cumene chromium,



v.p. at $82^\circ\text{C}.$ $\sim .05\text{mm}.$; obtained from Union Carbide Chemical Company, 30 East 42nd. Street, New York 17, New York.

- (3) Iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, v.p. at $18^\circ\text{C}.$ $\sim 28\text{mm}.$; obtained from Antara Chemicals, 435 Hudson Street, New York 14, New York.

- (4) Chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, v.p. at $26^\circ\text{C}.$ $\sim .43\text{mm}.$; obtained from Electro Metallurgical Company, Box 596, Niagara Falls, New York.

- (5) Nickel carbonyl, $\text{Ni}(\text{CO})_4$, v.p. at $30^\circ\text{C}.$ $\sim 330\text{mm}.$; obtained from International Nickel Company, 65 Wall Street, New York 5, New York.

Specimens were made from the following materials:

- (1) Nickel base alloy, Hastelloy R235.
- (2) Corrosion resistant steel, 17-7PH.
- (3) Titanium alloy, Ti 6Al 4V.

VI. APPARATUS:

A vacuum apparatus was built of pyrex glass for the manipulation of the toxic, and air reactive volatile compounds. It consisted of

VI. APPARATUS: (Continued)

condensation traps for storing and purifying metal compounds, a manometer, water cooled furnace, flowmeter, glass stopcocks, McLeod gauge, needle valve, hydrogen purifier, vacuum pumps, temperature recorder, an induction heater, and interconnecting glass tubing. Figure 1 shows a flow diagram of the apparatus, while Figures 2 and 3 are photographs of the essential features of the apparatus.

Design of the apparatus made it possible to operate at atmospheric or at reduced pressures with a maximum of safety. With the apparatus available the following variables could be controlled (1) vapor pressure of metal organics, thus changing the percent composition of the vapor in the carrier gas, (2) type and flow rate of carrier gas, (3) temperature of sample, (4) total pressure of the system and (5) time of plating or bonding.

VI. PROCEDURE:

A typical experiment consisted of scrubbing the specimen to be coated or bonded with soap and water and rinsing with methyl ethyl ketone. The specimen was then placed inside the water cooled pyrex induction furnace (approximately two inches in diameter).

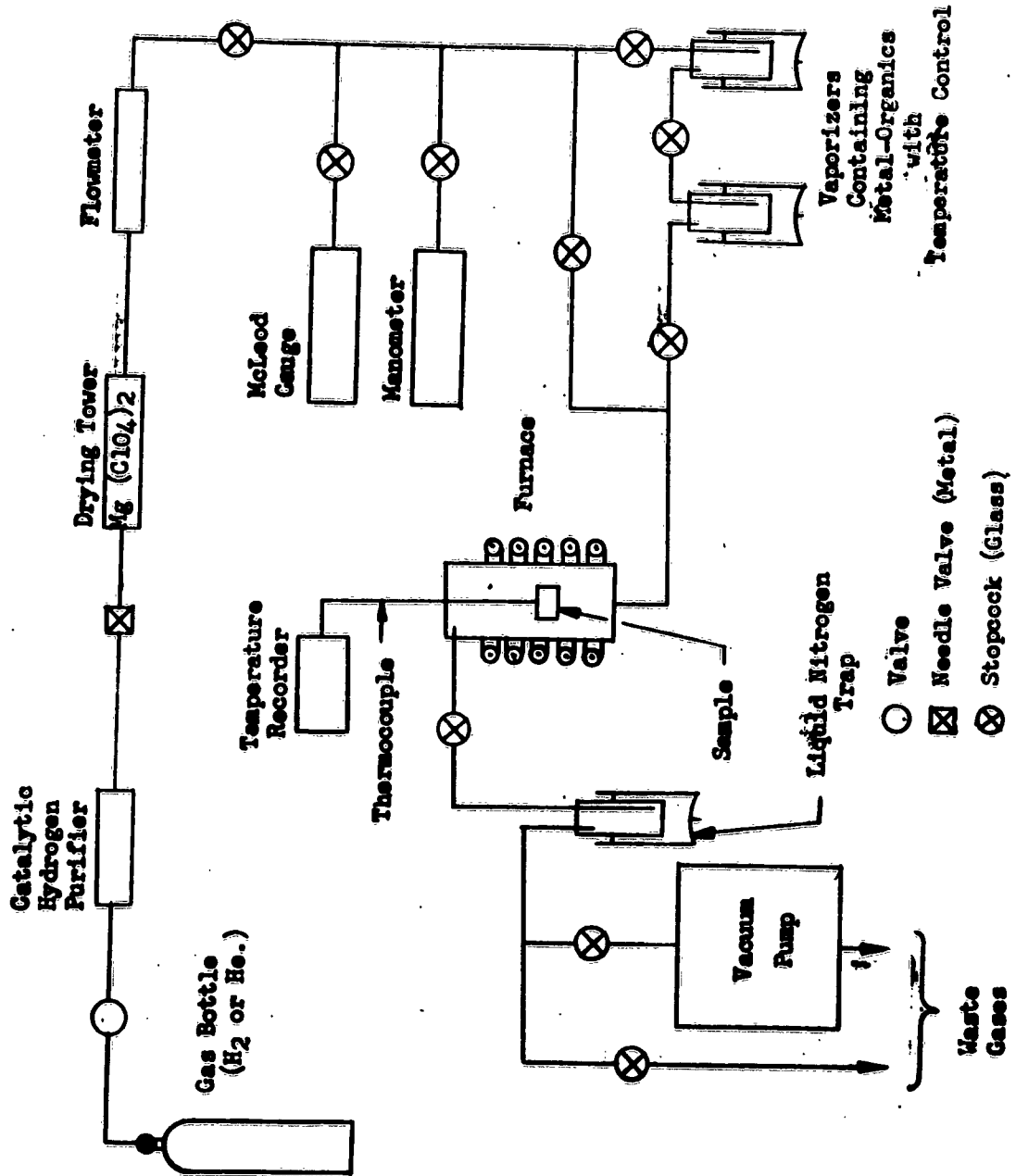


Figure 1. Schematic Diagram of Vacuum Apparatus

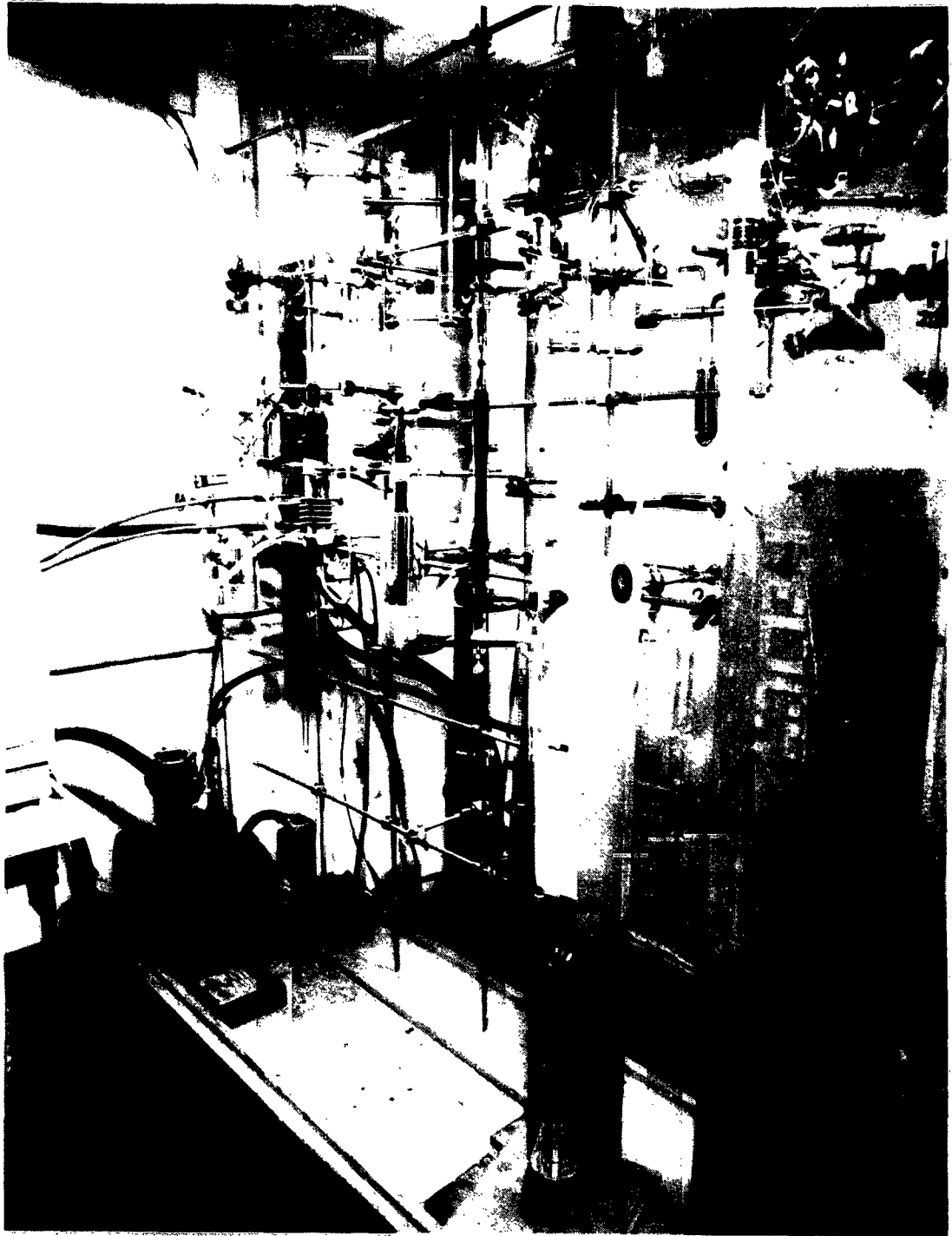


FIGURE 2 Front View of Vacuum Test Apparatus

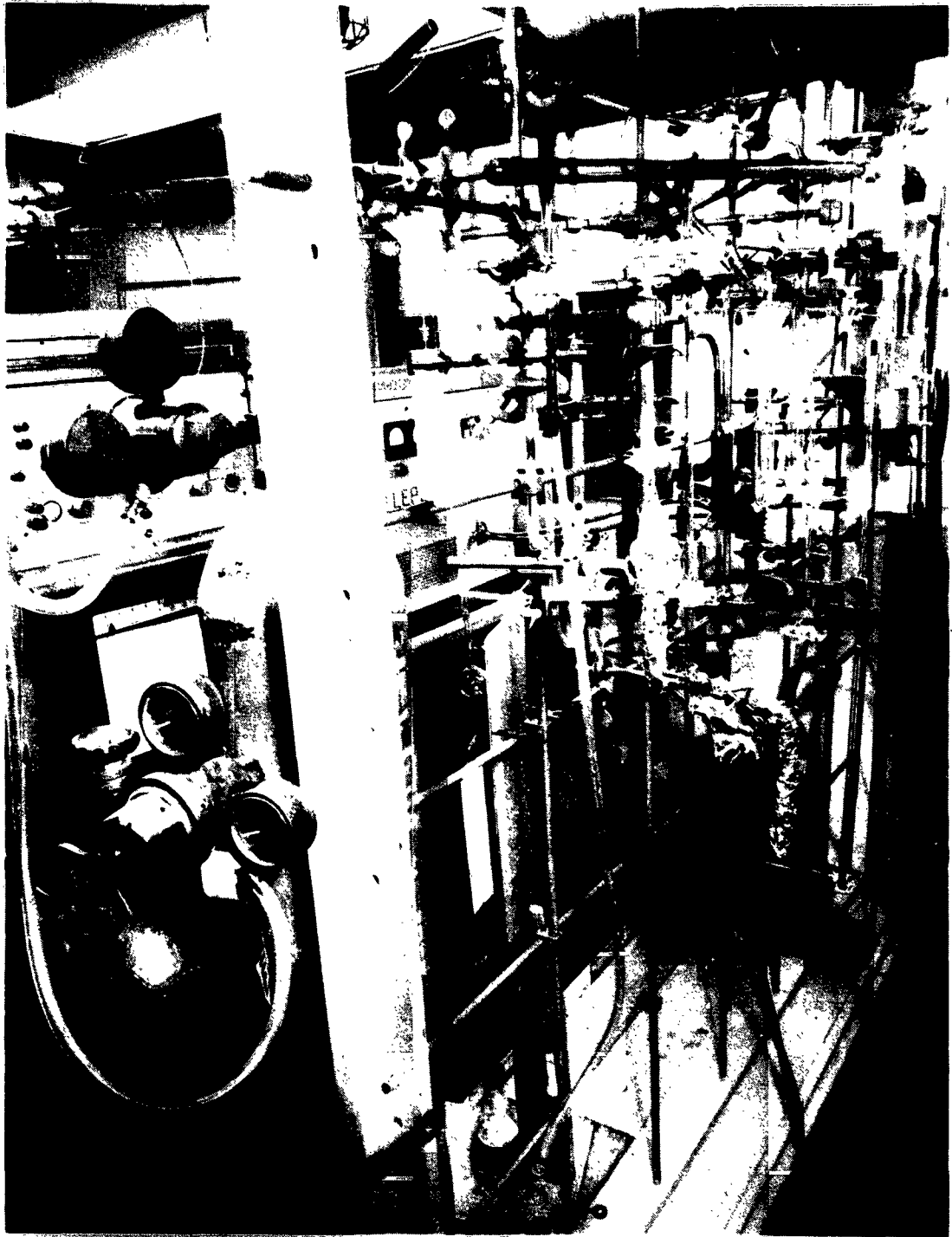


FIGURE 3 Rear View of Vacuum Test Apparatus

VII. PROCEDURE: (Continued)

The sample, located approximately in the center of the furnace, was held by means of a thermocouple which was connected to a recorder for indicating the temperature of the specimen. The specimen was heated by induced high frequency currents. External furnace heating was not employed as the plating efficiency would be low due to extreme deposition on the walls of the furnace.

The specimen was preheated in a hydrogen atmosphere to 650°C. to 700°C. for 15 to 30 minutes. This helped in the development of an adherent bond. The temperature was then lowered to the decomposition temperature of the metal organic and the specimen was maintained at this temperature while exposed to the "plating gas" consisting of a mixture of metal compound vapor and hydrogen or helium. This experiment could be performed at atmospheric pressure or at reduced pressure. An inert carrier gas, helium, was substituted for hydrogen in operations at atmospheric pressure. In operations at reduced pressure, a vacuum of approximately 1 μ was obtained previous to the introduction of the carrier gas. The metal compound was maintained at a specified temperature, as well as the specimen in the furnace. The carrier gas became "saturated" with vapor of the metal compound from the vaporizer, and the mixed gases entered the furnace. The temperature gradient in the furnace was as high as possible so that actual decomposition took place on the hot specimen and not on the walls of the furnace or in the gas phase.

VII. PROCEDURE: (Continued)

If decomposition occurred in the gas phase a "snowing" took place resulting in a non-adherent powdery coating. The reaction products, carrier gas, and undecomposed metal compound passed out of the furnace, with the undecomposed metal compound collecting in the liquid nitrogen trap. This trap also protected the furnace from oil and water vapor from the pump.

The sample was then annealed for 15 to 30 minutes at a temperature consistent with the materials being bonded. This heat treatment removed adsorbed gases, relieved stresses, generally increased the ductility, and decreased the tendency for the deposit to spall.

VIII. RESULTS AND DISCUSSION:

Initial experiments were designed to obtain the conditions of (a) flow rate, (b) temperature of specimen, (c) temperature of metal organic, (d) type of carrier gas, (e) annealing time, (f) cleaning conditions, and (g) total pressure of system (atmospheric to a few millimeters), in order to obtain a bond of nickel, iron and/or chromium to the base metal.

Other experiments followed in which the information learned initially was used in attempts to obtain bonding of 17-7PH alloy tee-joints and open face (half of a sandwich) honeycomb (17-7PH alloy) using nickel

VIII. RESULTS AND DISCUSSION: (Continued)

from nickel carbonyl and nickel obtained from the electroless method of aqueous solution plating. (See Figure 9).

Experiments were also planned to obtain a bonded layer of stainless steel (obtained from the gas phase mixture of nickel, iron, and chromium carbonyls) to the base metal. This according to the literature ⁴² is possible, however, time did not permit this group of experiments.

Good adherent ductile coatings of nickel and iron were obtained. (See Figures 4, 5, and 6). The ductilities and adhesion of the deposited coatings were determined on the basis of their ability to withstand severe bending. Ductile chromium and molybdenum deposits were harder to obtain, as seen from Figures 7 and 8. More experiments with chromium and molybdenum probably would result in increased ductility and less cracking.

Results of typical experiments for iron, chromium, nickel, and molybdenum, along with operating conditions, are listed in Table I.

TABLE I
OPERATING CONDITIONS FOR TYPICAL EXPERIMENTS

Metal	Organic	Flow rate Carrier Gas	Total Press. of System	Temp. & V.P. of Metal Organic	Cleaning	Time of Run Temp. of Sample	Annealing Conditions	Remarks
1.	Fe(CO) ₅	5 liters min. of H ₂	Reduced Press. ~74 mm.	0°C. -16mm. v.p.	Mechanically polished, wiped with M.E.K., heated in H ₂ 15 min. at 650°C.	20 min. at 40°C.	22 min. at 750°C. to 800°C. in H ₂	A diffused well bonded .0003" Fe plate on Ti 6Al 4V (See Fig. 6)
2.	Ni(CO) ₄	5 liters min. of H ₂	Atmospheric Press. of H ₂ .	0°C. -14mm. v.p.	washed in soap and H ₂ O, wiped with M.E.K., heated in H ₂ 14 min. at 650°C.	10 min. at 200°C.	23 min. at 425°C. in vacuum	A ductile, well bonded .00091" Ni plate on 17-7 PH alloy (See Fig. 4)
3.	Ni(CO) ₄	20 liters min. of H ₂	Reduced Press. ~18 mm.	-78°C. -20mm. v.p.	Wiped with M.E.K., heated in H ₂ for 10 min. at 650°C.	30 min. at 190° to 200°C.	15 min. at 425°C. in H ₂	A ductile, well bonded .0004" Ni plate on Ti 6Al 4V (See Fig. 5), which shows adherent plating on tension side of a bend specimen)
4.	Cr(CO) ₆	20 liters min. of H ₂	Reduced Press. ~100 mm.	50°C. -2mm. v.p.	Washed in soap and H ₂ O, wiped with M.E.K., heated in H ₂ 4 min. at 520°C.	60 min. at 225°C.	No anneal- ing	A brittle, adherent .0006" Cr plate on 17-7PH (See Fig. 8)
5.	Nb(CO) ₆	12 liters min. of H ₂	Reduced Press. ~20 mm.	50°C. 1mm. v.p.	Washed in soap & H ₂ O, wiped with M.E.K., heated in H ₂ 10 min. at 600° to 650°C.	70 min. at 320°C.	No anneal- ing	A brittle, adherent, .0013" Nb plate on 17-7PH alloy (See Fig. 7)



FIGURE 4 Cross section of .00091-inch nickel coating on 17-7PH alloy. Coating was deposited at atmospheric pressure in 10 min. Magnification: 500X. Etchant: acid ferric chloride.

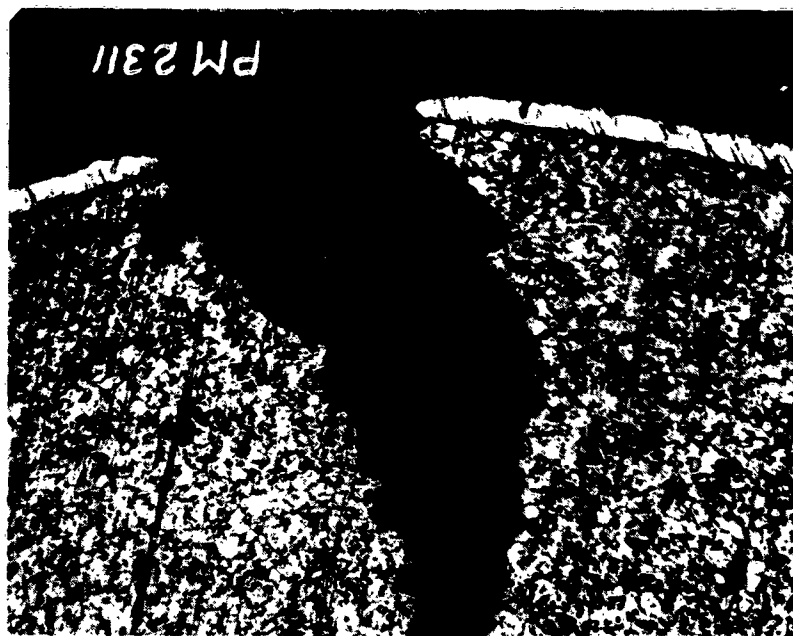


FIGURE 5 Cross section of .0004-inch nickel plate on Ti 6Al 4V sheet. View shows adherent plating on the tension-side of a bend specimen and crack propagating through parent material. Magnification: 400X. Etchant: acid ferric chloride.



FIGURE 6 Cross section of diffused .0003-inch iron plating on Ti 6Al 4V sheet. Magnification: 640X. Etchant: HF-H₂O₃.

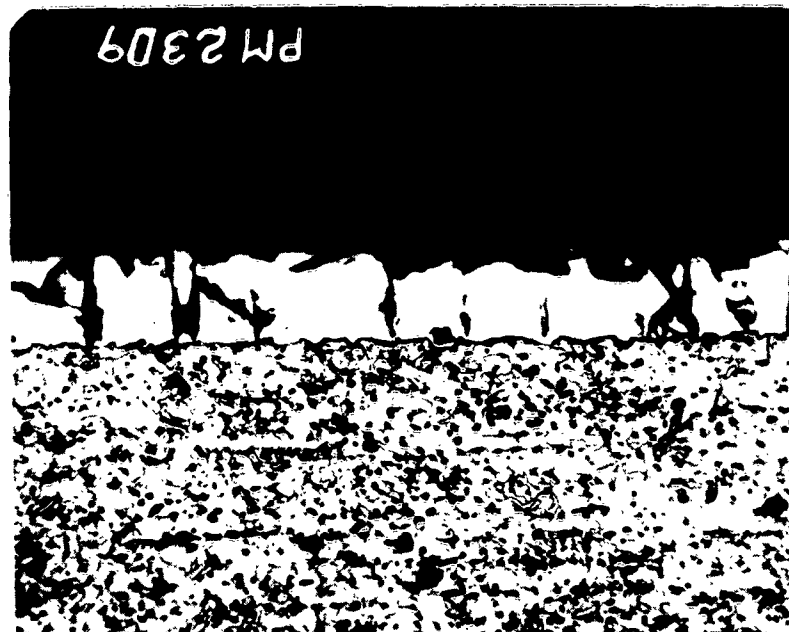


FIGURE 7 Cross section of brittle, adherent, .0013-inch molybdenum plating on 17-7PH alloy sheet. Magnification: 400X. Etchant: acid ferric chloride.

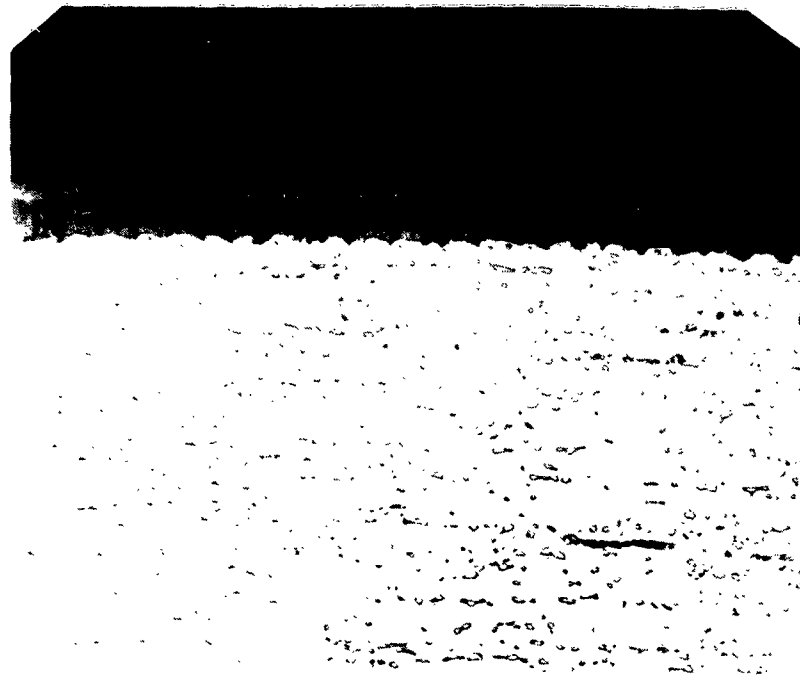


FIGURE 8 Cross section of brittle, adherent, .0006 inch chromium plating on 17-7PH alloy. Magnification: 500X. Etchant: HCl picric.

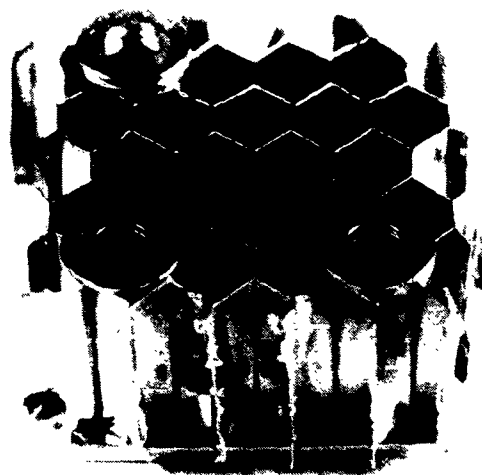


FIGURE 9 View of bonded honeycomb (facings and core are 17-7PH alloy). Structure was bonded by chemically reduced nickel from liquid solution. The visible washers were also fastened.

VIII. RESULTS AND DISCUSSION: (Continued)

Nickel deposited from nickel carbonyl gave the most ductile bond, the most easily reproduced bond, and the highest rate of plating. Thus, it was chosen for further experiments involving bonding of 17-7PH in tee-joints and open face honeycomb. Various attempts to join metal (17-7PH) by means of decomposition of nickel carbonyl were unsuccessful. Poor "throwing power" or inability to form a fillet were responsible. The deposited coatings became thinner near the tee-joint. An attempt to restrict the plating to a small area by masking with "Porcelox"* was also unsuccessful. Insufficient temperature drop through the mask caused deposition on the mask also. Other attempts to restrict the plating by using a nozzle to direct the vapor toward the position of the desired fillet also proved unsuccessful.

Some initial experiments were tried to determine whether plating could be accomplished in the inside cells of a honeycomb sandwich. Samples of stainless steel honeycomb with .08 inch holes connecting the individual cells were plated with nickel in a series of batch processes. These processes allowed the plating gas to reach the inside of the cells before the metal surfaces were heated to decompose the gas.

* (High temperature protective coating for metal surfaces; Kraus Research Laboratories, Cockeysville, Maryland.)

VIII. RESULTS AND DISCUSSION: (Continued)

After a batch or pulse of plating, the undecomposed gas and gaseous products of decomposition were pumped out of the system and a fresh charge of plating gas introduced to repeat the cycle. The resulting plated specimens were found to have plating on the walls of the interior honeycomb cells; however, no bond was observed between the metal honeycomb and the metal skins.

A private communication, with Dr. J. J. Lander of the Bell Telephone Laboratories, essentially confirmed our findings. Dr. Lander did the pioneering gas plating work with $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ (See Ref. 18). He stated that it would be difficult to bond two skins of steel in a tee-joint by pyrolysis of metal organics. He visualized difficulty with "throwing power" or ability to form a satisfactory fillet.

A telephone conversation with George S. Stoycos, Vice President of Commonwealth Engineering Company, Dayton Ohio, indicated that Commonwealth's experience with vapor phase metal bonding included the bonding of two nickel bars with nickel from the decomposition of nickel carbonyl. The nickel bars were separated by a gap of 1/4 inch, which was filled with nickel from $\text{Ni}(\text{CO})_4$ decomposition. The resultant bar had very good strength; he indicated that its strength was that of the original two nickel bars. G. S. Stoycos thought that the idea of bonding stainless steel honeycomb by metal organic decomposition was interesting,

VIII. RESULTS AND DISCUSSION: (Continued)

difficult, but possibly feasible. He stated that the first step of a feasibility study would be to arrange for a meeting of interested personnel from Convair and Commonwealth to discuss the problem further.

Other Approaches:

- (1) Induction Welding - In an attempt to bond 17-7PH stainless steel with nickel deposited from nickel carbonyl, it was observed that a weld was obtained at the interface of the metal (lap joint). At first it was thought that this bond was due to the nickel; however, metallurgical examination and further experiments proved that a weld resulted from induction resistance heating. Large currents had been induced in the metal and had caused high local heating at points of contact where the resistance was high. Attempts to reproduce this resistance welding proved successful. Joining metals by this method may warrant further investigation.

- (2) Metal Joining with Electroless Nickel - Initial attempts to join honeycomb sandwich (open faced sandwich) by an electroless nickel solution provided our first and only bonded sample of metal honeycomb. (See Figure 11). This method of plating insured uniform deposits of nickel in all areas, corners, crevices etc., wherever the solution came in contact with the base metal. Allowance was made for the release of hydrogen which was evolved by this process.

VIII. RESULTS AND DISCUSSION: (Continued)

A nickel plate (hardness, 500 vickers) of approximately .002 inches was obtained using an acid type electroless nickel bath. The bond formed by the core to the sheet was good, as the sample could be sawed in half without breaking the bond between the core and the sheet.

A more ductile nickel than that obtained on the test piece can be obtained by a post annealing of the plated specimen at a temperature of 750°F. in an inert atmosphere. Improvement of the metal bond can be made by use of honeycomb material of steel containing less chromium.

IX. RECOMMENDATIONS:

- (1) Commonwealth Engineering of Dayton Ohio, has spent 15 years on research and development in the field of gas plating. It is recommended that further contact be made with Commonwealth to discuss the matter of vapor phase bonding.
- (2) Vapor plating should be investigated as a means of producing plated parts without H₂ embrittlement.

IX. RECOMMENDATIONS: (Continued)

- (3) Take advantage of the fact that coatings made by vapor deposition, at high temperature, are frequently more adherent, less porous, and more stable under high temperature operation than materials deposited at lower temperatures by other methods.

- (4) Investigate, in more detail, the electroless nickel process for the production of high temperature resistant honeycomb.

- (5) Investigate induction resistance welding for the production of certain parts, and possibly for the production of high temperature resistant honeycomb.

X. CONCLUSION:

The results of our investigation indicate that certain factors appear adequate for the fabrication of metal honeycomb sandwich structures using metals from vapor deposition for the bonding agent. These factors include satisfactory adherent platings and a sufficient rate of plating in the case of nickel. To obtain plating inside a honeycomb cell, preliminary tests indicate batch wise plating or plating in pulses will allow plating where it could not be achieved by constant flow methods.

X. CONCLUSION: (Continued)

The investigation, also indicates that certain problems must be overcome before the process can be considered feasible. Major problems are the production of an adequate fillet and an improvement of the "throwing power." If these problems could be overcome, the success of the process would be greatly enhanced.

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