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CHEMICAL VAPOR DEPOSITION OF
ALUMINUM

Final Report

F. A. Clay, Project Leader

Project Team:
L. L. Lantz

Published August 1973

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**Kansas City
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CHEMICAL VAPOR DEPOSITION OF ALUMINUM

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Prepared by F. A. Clay, D/814

Chemical vapor deposition of aluminum was studied as an alternate process to electrodeposition. Using triisobutyl aluminum as the metal source, aluminum was deposited from both vapor and liquid onto both metallic and nonmetallic substrates. The visual appearance of the deposits obtained was good. Additional development of the process equipment would be required before these techniques could be used in production.

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SUMMARY

Chemical vapor deposition (CVD) of aluminum was investigated to determine its feasibility for plating aluminum on nonmetallic substrates to support product hardware. Triisobutyl aluminum (TIBAL) was chosen as the metal source. Visually good deposits were achieved on steel, stainless steel, aluminum, copper, polyimide, aluminum oxide, polysulfone, and graphite fibers. Apparently, any material can be plated that can withstand the 260°C plating temperature.

The effects on the deposit of substrate temperature, gas flow rates, gas ratios, and TIBAL vaporizer temperature were evaluated. The fastest plating rate and best looking deposits were obtained under the following conditions: 400 cm³/min nitrogen (inert atmosphere), 100 cm³/min isobutylene gas (TIBAL reaction control), 140°C TIBAL vaporizer temperature, and 260°C plating zone temperature.

Liquid phase deposition of aluminum from TIBAL was also studied. It was felt that this process would offer an increased plating rate over vapor deposition. By liquid phase deposition, 0.002 inch (50 μ m) of aluminum was deposited in a 20-minute period.

Although no full size parts were plated, success was obtained with both the CVD and liquid phase deposition. To go to a production operation, additional development would be needed on process equipment and controls.

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DISCUSSION

SCOPE AND PURPOSE

This report covers all of the work accomplished to date on the CVD of aluminum project. It was originated in June 1969 but work was not started until January 1971 because of insufficient facilities. The project was initiated at the request of LASL to develop a process for plating aluminum on non-metallic substrates. It was later expanded to include plating on graphite fibers for composites and pure aluminum coatings on various metal substrates.

PRIOR WORK

A variety of aluminum compounds have been investigated and used for thermal decomposition plating. These compounds have been applied to the substrates via the vapor, liquid, and solid phases. Vapor phase deposition is the most common and has been investigated more thoroughly than the others. Liquid phase deposition has only recently been used. Solid phase deposition has many difficulties and was not included in this project.

A literature search was conducted and revealed that aluminum trialkyls are most commonly used for thermal deposition; these, then, were selected for further investigation. A bibliography of the work on this subject is included in this report.

ACTIVITY

Preliminary Investigations

Based on the results of the literature search, the aluminum trialkyls appeared to be the best vapor plating compounds because of their relatively low decomposition temperature. Triisobutyl aluminum (TIBAL) was chosen because it was the least hazardous of the alkyls. Triisobutyl aluminum, however, reacts violently with water and is labeled as pyrophoric, meaning that it will ignite spontaneously on contact with air.

Since the literature indicated that this material is extremely hazardous, more information about its characteristics was required. A 10-cm³ sample of liquid TIBAL was placed in a dry glass-stoppered flask inside an inert atmosphere glove box. This sample was then transferred to a chemical hood

and exposed to the atmosphere to determine if it would spontaneously ignite. Although large volumes of dense smoke were evolved, there was no fire. A 25-cm³ sample was exposed with the same results. This test indicated that TIBAL is not pyrophoric in small quantities.

The manufacturers literature indicated that any amount of TIBAL could be rendered nonpyrophoric by mixing with at least three parts of a saturated hydrocarbon. Large quantities, up to 500 cm³, of TIBAL were disposed of by diluting it with toluene while it was under an inert atmosphere and then placing in a well ventilated hood. The diluted TIBAL reacted very slowly with atmospheric moisture and, within a few hours, was completely consumed.

Plating Chemistry

The following chemical reactions occur during thermal decomposition.

Reaction 1 occurs at about 100 to 150°C. During this step, TIBAL (a) is reduced to diisobutyl aluminum hydride (b) by releasing isobutylene gas (c). Then, at about 250°C, Reaction 2 occurs, during which the diisobutyl aluminum hydride (d) thermally decomposes to pure aluminum by releasing both hydrogen and isobutylene gas. Reaction 1 is reversible, and the formation of diisobutyl aluminum hydride (DIBAL-H) can be suppressed by adding excess isobutylene gas. Reaction 2 is not reversible.

In CVD plating, the aluminum plating material is carried into the plating chamber in the vapor phase. Since DIBAL-H has a low vapor pressure of about 4 mm Hg (530 Pa) at 140°C, it is impossible to obtain a sufficient amount of aluminum in the vapor stream to support plating. TIBAL has a higher vapor pressure of over 100 mm Hg (13.3 kPa) at 140°C, and thus allows a high enough aluminum content in the gas stream to support plating. Therefore, it is necessary to suppress reaction number one by adding isobutylene to the plating system. This ensures that the TIBAL is not reduced to DIBAL-H until after it is in the plating zone and ready for deposition.

CVD Plating System

The first laboratory setup (Figure 1) included dry nitrogen and isobutylene carrier gasses, a heated vaporizer containing about 100 cm³ of TIBAL, an infrared-heated plating chamber, and an acetone/dry-ice cold trap for the exit gasses. Precision flow meters were used to regulate the flow of the nitrogen and isobutylene. After mixing, the gasses were bubbled through the heated TIBAL liquid in the vaporizer. The TIBAL saturated vapor was then fed into the plating chamber, where deposition occurred. The spent gasses passed through an acetone/dry-ice cold trap to precipitate the isobutylene and any unreacted TIBAL. The remaining gasses were exhausted into a chemical hood.

Since Crosby¹ had successfully vapor plated aluminum using a nitrogen-isobutylene ratio of 8.5 to 1, the first run was made using this ratio. A short length of copper wire was cleaned and placed in the plating chamber. The system was purged for 15 minutes with dry nitrogen before attempting to plate. After purging, the isobutylene was turned on and the vaporizer bypass valve was closed to permit TIBAL vapor to enter the plating chamber.

This run resulted in both aluminum and carbon being deposited on the walls of the glass chamber. The glass chamber had apparently become overheated while the copper wire was being heated. A second run was made using air cooling of the plating chamber walls, but no plating occurred. This, like the previous run, indicated that the glass was absorbing the infrared (IR) energy to the extent that the copper wire was not getting hot.

The IR heating was then replaced with zone heating. A resistance heating tape was wrapped around the glass tube of the plating chamber to form the hot zone. Visually good deposits were produced using this system, although some TIBAL was wasted; both the plating chamber walls and the wire were coated. This system was then modified by inserting a copper tube between the heating tape and the glass tube. This change allowed a better heat distribution across the length of the tube.

Since this system appeared capable of holding a reasonable tolerance on the plating temperature, it was decided to evaluate the effects of varying the process controls.

¹ J. J. Crosby, Vapor Plating of Aluminum on Steel. Wright-Patterson AFB, Ohio: ASD Technical Documentary Report 62-097, Air Force Systems Command, 1962.

Figure 1. CVD Plating Setup

CVD Plating Studies

Plating temperature effects were studied, and it was found that the lightest colored and smoothest deposits were obtained at temperatures ranging from 240 to 260°C. The deposit was gray when plated at temperatures outside this range. The shade of gray varied as the temperature deviated from optimum; larger differences caused darker deposits. At high temperatures, the deposit was gray and rough due to carbon inclusions. At low temperatures, the deposit was gray but smooth. The low temperature color change was probably the result of a somewhat incoherent deposit that was very fine grained. At about 220°C the deposit became powdery and incoherent.

Both the total gas flow and nitrogen-to-isobutylene ratio were also varied to evaluate their effect on plating rate and deposit appearance. The total gas flow did not measurably affect the plating rate until it became either large enough to lower the temperature in the plating zone or low enough to starve the plating chamber for TIBAL. The cooling effect in this system was observed at total flow rates above 650 cm³/min in a 12-mm-diameter-tube plating chamber. The test indicated that total flow is not an important item to control.

The amount of isobutylene in the carrier gas was not found to be significant as long as it was kept above a minimum value. The minimum value depended on the temperature of the liquid TIBAL in the vaporizer. If the isobutylene flow was too low, the TIBAL became converted to DIBAL-H in the vaporizer. Because of the low vapor pressure of DIBAL-H, very little aluminum was then carried to the plating chamber. This condition was readily seen in the top of the glass vaporizer. When sufficient isobutylene was present, the vapor area was very cloudy. This area became clear when the isobutylene was too low. Isobutylene to nitrogen ratios up to 1 to 1 did not affect plating rate or deposit appearance as long as there was sufficient isobutylene to prevent formation of DIBAL-H. Higher isobutylene contents were not evaluated.

Vaporizing temperatures of 100 to 140°C were evaluated. The higher temperatures resulted in more TIBAL being carried to the plating chamber, thus increasing the plating rate; but, as stated previously, the isobutylene flow had to be adjusted because of the temperature variation. Temperatures lower than 100°C were not evaluated because of the low vapor pressure of TIBAL at these temperatures. Higher temperatures also were not evaluated because of breakdown products that precipitated from the liquid TIBAL.

The fastest plating rate obtained using this system was 1.2 mil/hr (30 μm/hr). This rate was achieved using the following conditions: 400 cm³/min nitrogen, 100 cm³/min isobutylene, a vaporizer temperature of 140°C, and a plating zone temperature of 260°C.

It is thought that a higher plating rate could be obtained by preheating the gas prior to its entering the plating zone and adding a flash vaporizer for the TIBAL. These changes would result in a higher TIBAL content in the plating chamber and, therefore, a faster plating rate. Although this was not tried because of a lack of equipment, all previous work indicates that the plating rate is primarily determined by temperature and TIBAL concentration in the plating chamber.

Several types of substrates were aluminum plated using this system (Figures 2, 3, and 4). The nonmetallics did not plate as uniformly as the metals because poorer thermal conductivity resulted in surface temperature variations. However, good appearing deposits were obtained on steel, stainless steel, aluminum, copper, polyimide, aluminum oxide, polysulfone, and graphite fibers. Standard aqueous techniques could be used to clean copper and low carbon steel well enough to achieve adherent deposits. The other materials had to be vapor blasted to obtain adherence.

Liquid Phase Plating Studies

Some liquid phase deposition studies were made in an attempt to produce an aluminum coating on a nonmetallic substrate that could then be anodized. Since the deposit had to be at least 0.002 inch (50 μm) thick, liquid phase deposition was more attractive for this application than vapor plating because it had the potential of producing this thickness in a shorter time.

Immersing a heated specimen in the TIBAL liquid resulted in boiling but very little plating. Spraying the surface of a heated panel with TIBAL using a perfume atomizer was fairly successful. Good looking but thin deposits were produced. Again, most of the liquid boiled away before decomposing. A third method produced better results. In this test, a Buchner funnel was inverted over the heated panel, a buret was inserted in the funnel stem, and steel wool was lightly packed in the stem opening. TIBAL was metered dropwise into the heated area using the buret. The plugged funnel restricted the vaporized TIBAL preventing it from escaping from the plating area. Using this system 0.002 inches (50 μm) of aluminum was deposited in a 20-minute period.

The liquid phase studies indicated that thick aluminum deposits could be produced in a relatively short time, but that a better material handling system was needed to prevent excessive usage of TIBAL. A liquid spray coating system using DIBAL-H might be the most practical. This idea was not pursued because of project priority changes.

Figure 2. CVD Aluminum on Polyimide, 1000X

Figure 3. CVD Aluminum on Stainless Steel, 1000X

Figure 4. CVD Aluminum on Stainless Steel Bolt

ACCOMPLISHMENTS

Aluminum was successfully chemical vapor deposited on substrates of steel, stainless steel, aluminum, copper, polyimide, aluminum oxide, polysulfone, and graphite fibers. Using liquid phase plating, a plating rate of 0.006 inch (150 μm) per hour on a nonmetallic substrate was achieved. Also, various metallic substrates were plated and anodized.

Although a basic process capable of plating product hardware was developed, facility limitations precluded processing of full-size parts. It had become apparent that a larger and more sophisticated system would be required for plating production hardware when work on this project was terminated. Activity ceased before a new system could be assembled.

It is felt, however, that enough information has been obtained that a reliable plating system could be built. The thermal decomposition plating process shows much promise for aluminum coating the surface of any material that will withstand 260°C.

FUTURE WORK

Future work related to this project should include both liquid phase deposition studies using DIBAL-H and construction of a more sophisticated plating system. The new system should include an induction heater for metallic substrates and a zone or microwave heater for nonmetallic parts. Also, a new vaporizer is needed to accurately control the amount of TIBAL in the carrier gas. A TIBAL recycling system would be desirable for larger parts.

Liquid phase deposition using DIBAL-H should be investigated as a means of building thick deposits rapidly. The vapor equivalent of electroforming should also be evaluated.

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