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CVD ALUMINUM PLATING ON STEEL

By F. A. Clay

Published January 1979

Final Report

Prepared for the United States Department of Energy
Under Contract Number DE-AC04-76-DP00613.

**Kansas City
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Final Report
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A chemical vapor deposition (CVD) process was developed that produces aluminum coatings capable of being anodized at 500 volts. The intent is to use this method to apply an anodized coating onto the interior of a complex-shaped part. Unrecycled TIBAL, one of the least pyrophoric of the alkyls, was used under the following optimum coating conditions: temperature, $260 \pm 5^\circ\text{C}$; spray pressure, $345 \pm 35 \text{ kPa}$; and time, 2 to 3 hours.

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SUMMARY

A chemical vapor deposition (CVD) aluminum plating process has been developed that will produce coatings that can be anodized to 500 volts. Test results of the anodized coating are comparable to similar data taken for a solid barrier anodized 6061 aluminum alloy part. The best coating conditions for the alkyl-unrecycled TIBAL are as follows: temperature, $260 \pm 5^{\circ}\text{C}$; spray pressure, 345 ± 35 kPa; and time, 2 to 3 hours.

DISCUSSION

SCOPE AND PURPOSE

The development of a Chemical Vapor Deposition (CVD) process was needed for applying an aluminum coating, that could be anodized, onto a steel substrate. The CVD process was selected because the complex shape of certain parts made alternative coating methods impractical.

PRIOR WORK

This process development order was oriented toward aluminum coating of graphite fibers for composite applications and coating of other parts for corrosion protection or for special applications. No anodizing was done during this project. The objective was to assess the feasibility of CVD coating aluminum onto steel substrates, but funding limited optimizing the plating parameters and characterizing the resultant coatings.

ACTIVITY

Background

For some parts requiring an anodized aluminum coating on interior surfaces, CVD appears to be the only feasible coating method. The complex shape of these steel parts seems to make electroplating, vacuum coating, or bonding of a liner impractical as coating methods.

Aluminum coatings can be easily produced by the thermal decomposition of aluminum alkyls.* Triisobutylaluminum (TIBAL) and diisobutylaluminum hydride (DIBALH) were used in this work because they are the least pyrophoric of the alkyls, and experience had been gained with TIBAL on previous CVD plating activities. These compounds also will thermally decompose (plate) at the lowest substrate temperatures.

*Powell, Oxley, and Blocher. Vapor Deposition. New York: John Wiley and Sons, 1966, pp. 277-283.

Chemistry and Safety

TIBAL and DIBALH are very reactive, clear liquids at room temperature. They will ignite spontaneously when exposed to air and react violently with water. Therefore, they must be contained in a dry inert atmosphere, such as argon or nitrogen. For disposal, these materials can be diluted with a saturated hydrocarbon, such as kerosene, to render them nonpyrophoric. The diluted material can then be disposed of like other flammable wastes.

TIBAL and DIBALH undergo thermal decomposition reactions, as follows, at about 250°C.

TIBAL

DIBALH

Aluminum can be deposited on any metallic or nonmetallic surface that can be heated to the decomposition temperature.

Equipment

The equipment used in this work (Figure 1) was designed to allow safe handling and disposal of aluminum alkyls. This system is purged with nitrogen and kerosene before the alkyl is introduced into it. Thereafter, it is kept under a slight positive pressure of dry nitrogen to ensure against air leakage into the system.

The plating system has four main sections: the induction heater, the plating chamber, the material handling section, and the waste disposal section.

The induction heater is a 2-kVA power supply that was used to heat the parts to the desired plating temperature. It is a manually-controlled unit. The part temperature was monitored continuously during coating, using a thermocouple and recorder.

Figure 1. CVD Aluminum Plating System Schematic

The plating chamber is a standard 152-mm glass cross that has a spray nozzle mounted in two of the legs. An induction heating coil is mounted through the third leg, and the fourth is used for parts to be passed in and out through a gate valve and pass box with a dry nitrogen purge.

The material handling section consists essentially of a variable-speed pump and pressure bottle system whereby the alkyl can be pressurized, sprayed on the part, and recycled until consumed or disposed of. The variable-speed pump allows pressure control ranges of 200 to 900 kPa. Kerosene can also be introduced into this system and recycled, as desired, to clean it out for extended storage or repair.

A modified safety can is used for waste disposal. It is kept about one-half full of kerosene. All vent gases are run through this can prior to exiting into the chemical hood. Spent alkyl is put into this can for dilution to nonpyrophoric concentration before disposal. When full, the diluted alkyl is drained into a special pressure container that is under a nitrogen atmosphere. The container is then sealed and shipped out for disposal.

Coating Process

Only low-carbon steel panels, approximately 100 by 100 by 0.8 mm, were plated during this project because of size limitations of the present CVD equipment. All panels were degreased and vapor blasted with aluminum oxide prior to plating. It had been found that this process promoted good adherence of the vapor deposited coating to a steel substrate during the earlier CVD aluminum work.

After cleaning, the panels were attached to a low-carbon steel plate, 100 by 100 by 6.3 mm, fastened to a holding rod that contained a thermocouple positioned to provide intimate contact with the panel surface, and loaded into the purge chamber of the plating system (Figure 1). After purging a panel with nitrogen, the gate valve was opened and the panel was lowered into the plating chamber, using the holding rod. The panel was held parallel to a flat, spiral induction coil in the plating chamber, using a fitting with a Teflon bushing.

Previous work has been done using the thin 0.8-mm steel panels without the backup plate. That work had shown a plating thickness variation which was larger than desirable across the panel, and the temperature had fluctuated rapidly during deposition because of its small mass. Therefore, a backup plate was used in this work to overcome these problems. The induction coil and coating position were the same as those developed earlier.

When in position, the induction current was activated and the panel was heated to the desired coating temperature, usually 250 to 270°C. When at temperature, the aluminum alkyl was atomized and sprayed onto the hot surface to initiate deposition. The spraying/heating process continued until the desired thickness of aluminum was produced. The unreacted alkyl was recycled continuously during the run.

When the plating was completed, the spray and induction heating were stopped. The panel was raised into the purge chamber, and the large gate valve was closed. After purging, the part was removed from the plating system, removed from the holding rod and backup plate, and stored in a plastic box until anodized.

Coating Process Variables

Two aluminum alkyls, TIBAL and DIBALH, were selected in this project. TIBAL was used because it plates at low substrate temperatures and is less pyrophoric than lower molecular weight alkyls. DIBALH was selected because it is similar to TIBAL in safety and deposition temperature, but has a much lower vapor pressure. It was thought that the lower vapor pressure might produce superior coatings in a liquid spray system.

Addition of isobutylene gas to the plating chamber during deposition was evaluated with each of the above alkyls. Isobutylene is released during the coating process, so it was desirable to determine if the addition of extra isobutylene would improve certain coating characteristics such as porosity.

Panel plating temperatures of 250 to 300°C were investigated. Previous work had shown that temperatures outside of these limits produce powdery, noncoherent coatings.

Alkyl spray pressures and coating times were varied to change the plating rate and coating thickness. An attempt was made to optimize these variables to produce a pore-free coating.

Anodizing Process

Because the purpose of aluminum plating the steel was to produce a coating that could be anodized, the anodizing operation was used to determine the quality of the coating. Initially, all anodizing work was done at 500 volts in a solution containing 7.5 grams of ammonium tartrate, 750 milliliters of DI water, and 2250 milliliters of ethyl alcohol. A later sample was anodized at 1000 volts in a similar solution, because of a change in design requirements; but no 1000-volt data will be presented in this report because it was not investigated sufficiently to produce reliable data.

Prior to being anodized, the aluminum-coated panel was loaded into a special fixture that made electrical contact to the uncoated side of the panel but protected it from solution contact. The fixtured part was then loaded into the anodizing solution and connected to a dc power supply. The part was connected to the anodic lead, and the cathode lead was connected to a platinum panel in the anodizing solution. The power supply was a constant voltage/constant current instrument with automatic crossover. After loading, the power supply was turned on, and the initial current was set at 100 mA. As the anodizing progressed, the voltage would increase to 500 volts at which time the voltage would remain constant and the current would decay towards zero. The process was maintained until the current reached a stable value. At this point, the anodizing was stopped, and the fixture was removed from the solution. The panel was removed from the fixture, flushed with clean ethyl alcohol, and stored in a dust-free box.

Any porosity in the aluminum coating resulted in panels that would not anodize. They either would not reach 500 volts, or the current would not decay to less than 50 mA.

Results

The coating conditions are listed in Table 1 for most of the 30 panels plated during this project. Some panels have been omitted because of equipment malfunctions during a coating run, and others because anodizing data were not taken when the coating was obviously too dark and clumpy to provide good results.

As shown by Table 1, TIBAL produced a better anodized coating than did DIBALH. The addition of isobutylene is not satisfactory for producing a coating that will anodize.

Figures 2 through 5 are scanning electron microscope (SEM) photomicrographs of aluminum deposits at various plating conditions (Table 1), which verify that TIBAL deposits have a more uniform grain structure than those produced with DIBALH. Figures 2 and 3 are TIBAL deposits. Figure 4 is a TIBAL deposit produced with the addition of isobutylene gas to the plating system, and Figure 5 is a DIBALH deposit. As shown, the TIBAL deposits have a fairly uniform grain size and texture, while the TIBAL with isobutylene and the DIBALH deposits are clumpy and nonuniform. Figures 6 and 7 show cross sections of a deposit from each alkyl. These photomicrographs also show that the TIBAL deposits are smoother and more uniform than the DIBALH deposits.

Based on this work, the best deposition temperature was found to be about $260 \pm 5^{\circ}\text{C}$, and the best spray pressure was about 345 ± 35 kPa. The best coatings were obtained by using new TIBAL.

Table 1. Coating Conditions

Panel	Temperature	Spray Pressure (kPa)	Coating Time (min)	Alkyl Type*	Gas**	Anodizing		Coating Appearance
						Volts (max)	mA (min)	
50	255-260	550-620	120	T*	None	500	44	Smooth, matte, white
51	280-285	550-620	60	T		130	100	Rough, dark
52	255-260	550-620	60	T		500	83	Smooth, matte, white
53	255-260	550-620	90	T		150	100	Darker than 52
54	255-260	550-620	60	T	None	500	26	Darker than 52
55	255-260	550-620	60	T	5 cfh	60	100	Rough, thick
56	255-260	550-620	60	T*	5 cfh	60	100	White, smooth
57	255-260	550-620	60	T	1 cfh	80	100	White, smooth
58	255-260	550-620	60	T	None	360	100	White, smooth
59	255-275	550-620	60	T	None	60	100	Dark corner
61	270-275	310-380	60	T	1 cfh	(Damaged, Not Anodized)		Dark corner
62	270-275	550-620	60	T	1 cfh	120	100	Rough, dark
63	260-265	310-380	105	T	None	90	100	Uniform gray
65	270-275	310-380	95	T	5 cfh	20	100	Uniform gray
66	250-255	380-450	120	T*	None	500	30	Smooth, gray-white
67	250-255	380-450	120	T	None	(Coating Damaged, Scratched)		Smooth, gray-white
69	255-260	310-380	135	T*	None	500	9	Smooth, white
70	255-260	310-380	135	T		180	100	Dark center area
71	260-285	310-380	135	T		500	10	Smooth, white
73	260-285	310-380	135	T				Thickness sample
75	260-265	310-380	40	D	None			Spray clogged, rough deposit

Table 1 Continued. Coating Conditions

Panel	Temperature	Spray Pressure (kPa)	Coating Time (min)	Alkyl Type*	Gas**	Anodizing		Coating Appearance
						Volts (max)	mA (min)	
76	260-265	690-760	60	D	None	20	100	Rough dark deposit
77	250-255	690-760	30	D	None			Rough dark deposit
78	250-255	690-760	30	D	1 cfh			Rough dark deposit

T is recycled TIBAL, and T is new TIBAL; D is DIBALH.

**Isobutylene

2A. SEM 300X

2B. SEM 3000X

Figure 2. Aluminum Deposited From
TIBAL, Panel 52

3A. SEM 300X

3B. SEM 3000X

Figure 3. Aluminum Deposited From
TIBAL, Panel 66

4A. SEM 300X

4B. SEM 3000X

Figure 4. Aluminum Deposited From
New TIBAL, Panel 55

5A. SEM 300X

5B. SEM 3000X

Figure 5. Aluminum Deposited From
DIBALH, Panel 77

Figure 6. Aluminum Deposited From
TIBAL, Panel 66 (SEM 500X)

Figure 7. Aluminum Deposited From
DIBALH, Panel 77 (SEM 500X)

The deposits became worse as the TIBAL was recycled through more than one panel. Also, the visual appearance of the panel was fairly indicative of its anodizing performance. The panels that were a matte, smooth, white color anodized better than did the grayer or rougher deposits.

Four anodized panels were processed into simulated parts and were electrically tested. Final test results of these parts showed that they had leakage currents typical of 6061 aluminum alloy panels processed in a similar manner.

From the data obtained during this project it appears that with the CVD process, aluminum coatings can be produced that will withstand a 500-volt anodizing process and that functional parts can be produced. However, the product requirements have been changed recently to specify a 1000-volt anodize coating, and more data are needed to determine if the CVD process can be used to produce an aluminum coating that will withstand this new requirement.

ACCOMPLISHMENTS

A CVD process was developed that produced aluminum coatings capable of being anodized at 500 volts. The optimum coating conditions for the alkyl-unrecycled TIBAL are as follows: temperature, $260 \pm 5^{\circ}\text{C}$; spray pressure, 345 ± 35 kPa; time, 2 to 3 hours.

FUTURE WORK

The change in anodizing requirements from 500 to 1000 volts will require additional development work. Most of the baseline processing conditions, such as temperature, spray pressure, and alkyl type should remain the same; but the porosity and thickness of the aluminum coating will have to be changed to withstand the 1000-volt anodizing. Also, coating of complex shapes needs to be investigated.

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SPECIAL PROJECTS: Chemical Vapor Deposition

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