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ALUMINUM PLATING GRAPHITE FIBERS
AND BERYLLIUM WIRE

PDO 6984714, Final Report

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**Kansas City
Division**

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Prepared by F. A. Clay, under PDO 6984714

Metal-matrix composites required continuous lengths of aluminum-coated graphite fibers and aluminum-coated beryllium wire. Although short lengths of graphite fibers were successfully plated with aluminum using a CVD batch process, continuous plating was not accomplished because of insufficient process control. A fixture and process were developed for the continuous electroplating of 0.005-inch diameter (127 μm) beryllium wire. A diethyl ether aluminum plating bath was used. Continuous lengths up to 20000 feet (6.1 km) were plated. A total of 505000 feet (154 km) were processed.

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KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

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SUMMARY

Attempts were made to deposit aluminum on continuous lengths of both graphite fibers and beryllium wire. Aluminum was successfully chemically vapor deposited (CVD) on small batches of graphite tow using triisobutyl aluminum, but all attempts to establish a continuous process were unsuccessful. A plating system having better controls, more uniform heating and some type of yarn spreading feature would be needed to establish a continuous process. Electroplating of aluminum on graphite fibers was also attempted without success. The throwing power of the plating process did not allow penetration of plating into a fiber bundle. Only the outer fibers were coated. If the fibers could have been spread into a tape configuration, then electroplating might have been feasible.

A process for plating continuous lengths of beryllium wire was established. Static plating tests were made with short lengths of 0.005-inch diameter (127 μm) beryllium wire to establish the plating conditions. The results were used to design and build a fixture having a continuous plating capacity of about 1000 feet (305 m) of wire per week. Over 5000 feet (1524 m) of wire were plated in this fixture. A second generation, larger capacity wire plater, was then designed and built.

Using two second-generation platers, 500000 feet (152 km) of wire were plated in seven months. Each plater had a capacity of about 15000 feet (4.6 km) per week based on a 0.001-inch thick (25 μm) aluminum coating. They were operated continuously, requiring operator attention only during the first 2 hours of each work day.

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DISCUSSION

SCOPE AND PURPOSE

The objective of this project was to develop a process to aluminum coat continuous lengths of graphite fibers and beryllium wire. The plated material was to be used in the development of metal-matrix composites.

This work was done from June 1970 to March 1972 to support a Sandia Albuquerque paid order.

PRIOR WORK

The aluminum electroplating process was developed under PDO 6984228; the CVD process was developed under a previous process development order.

ACTIVITY

Plating Graphite Fibers

The graphite fiber plating investigation was limited to tow (untwisted fibers) and Thornel 75[®]. The Thornel yarn (twisted fibers) has a higher modulus and fewer fibers per strand, but since it is twisted it is much more difficult to spread for plating infiltration.

Short lengths of both types of fibers were cleaned with acetone to remove the polyvinyl alcohol coating, dried and electroplated in the diethyl ether aluminum plating solution.¹ These tests indicated that aluminum would deposit on the fiber surface, but because of the poor throwing power of this bath, only the outer fibers were plated (Figure 1). Since it was not feasible to spread the Thornel yarn, only the tow was used for further electroplating tests.

In another test, short lengths of tow were wound on a wire rack, spread by hand to a tape configuration, cleaned, dried, and plated. By varying the current density it was found that good aluminum deposits could be obtained on the

[®]Union Carbide Company.

¹F. A. Clay, W. B. Harding, and C. J. Stimetz, "Aluminum Plating," Plating, Volume 56, Number 9, September, 1969, pp 1027-1037.

spread tow at 15 to 20 Asf (161 to 216 A/m²). The best penetration and best looking deposits occurred at the point of contact between the copper wire rack and the graphite tow probably because of the better conductivity of the copper.

Figure 1. Cross Section of Aluminum Plated Graphite Yarn (320X)

Using a small laboratory CVD setup, 0.10-meter lengths of tow and yarn were batch plated with promising results. These samples had been spread by hand into a loose bundle to allow the aluminum alkyl vapor free access through the strands. Although the aluminum deposit was thicker than desired, there was better penetration of the plating (Figure 2). These results looked so encouraging that the electroplating investigation was dropped in favor of the CVD approach.

In the CVD process, aluminum will deposit from triisobutyl aluminum (TIBAL) vapor onto any surface hotter than 480°F (249°C). The best looking deposits occur at 480° to 500°F (249° to 260°C). At lower temperatures the plating rate is very slow and the deposit is powdery; at higher temperatures the deposit becomes dark and very rough with carbon inclusions.

Resistance heating, zone heating, and infrared heating were evaluated as methods of holding the graphite fibers within the desired temperature range. Resistance heating heated the center of the fiber bundle first, causing aluminum to deposit only on the heated fibers. After deposition began, the aluminum

SIDE VIEW (300X)

END VIEW (200X)

Figure 2. Side View and End View of Plated Graphite Tow

plated fibers apparently carried all of the heating current because of their lower resistance; this prevented the uncoated fibers from becoming plated. Zone heating resulted in wasted material because the walls of the plating chamber were coated along with the outer fibers of the bundle. There was some penetration into the bundle but not as much as desired. The lack of plating in the center probably resulted from the temperature gradient across the bundle and insufficient gas flow within the bundle. Infrared heating was not successful since it was difficult to control and eventually resulted in plating on the glass chamber preventing further heating of the yarn. Induction heating of the graphite fibers was evaluated but was not successful because of insufficient mass of the fibers.

Several simple batch and continuous setups were evaluated in an attempt to produce 10 foot (3 m) minimum lengths of coated fibers. The best batch results were obtained using zone heating. The graphite tow was hand formed into a loose, porous ball, placed in the heated zone, and the TIBAL vapor was forced through the fibers. About 70 percent of the available fibers were plated using this technique, but heating variations caused a large variation in plating thickness. A combination of resistance and zone heating produced the best results for a continuous process. In this setup the tow was spread into a tape configuration using an air jet; it then passed through copper rollers, an inert gas curtain, a zone heated plating chamber, another gas curtain, a second set of copper rollers, and onto a spool (Figure 3). The copper rollers kept the spread tow held in a tape configuration and provided the contact for resistance

Figure 3. Resistance and Zone Heating Plating Process

heating. The gas curtains prevented TIBAL from contacting the atmosphere. The plating chamber was zone heated to 420°F (216°C) just below the deposition temperature. Resistance heating was used to raise the temperature of the fibers to 480°F (249°C) to 500°F (260°C). Again, not all of the fibers were plated and there was a large thickness variation from fiber to fiber.

It became apparent during these tests that a more sophisticated setup was needed. These simple setups did not have a reliable, uniform heating system or adequate process controls to ensure repeatable results. This phase of the project was stopped before a reliable system could be developed.

Plating Beryllium Wire

The beryllium wire plating activity on this project consisted of four sequential subactivities: study of beryllium activation; design, construction, and testing of a prototype plater; design, construction and testing of a production plater; and plating the wire.

A naturally occurring oxide coating prevents beryllium from making direct contact with a plated metal. Direct contact is essential for a fully adherent coating. A metal coating applied over the oxide is primarily bonded to the substrate by mechanical interlocking and thus has a lower level of adhesion. Maximum adhesion was necessary; therefore, activation processes were studied to achieve metal-to-metal contact.

Several preplating processes were evaluated but only one gave a deposit that could not be peeled with a razor blade. The original wire before preplating is shown in Figure 4 and examples of preplating are shown in Figure 5. The successful process was a solvent clean followed by a reverse etch in the plating bath at 250 Asf (2690 A/m²) prior to plating. A fairly good bond was obtained using a 5 percent sulfuric acid etch pretreatment to roughen the surface. Chemical polish and electropolish treatments gave poor adhesion because the surface was too smooth. However, during this study, Sandia found that a mechanical bond was sufficient because it could be converted to a strong, metallurgical bond during the heat and pressure cycle used to form the metal composite. The cleaning of the bare wire was, therefore, limited to a solvent wipe with isopropyl alcohol.

The first Sandia order was for 5000 feet (1524 m) of plated wire, in minimum lengths of 1000 feet (305 m), containing between 50 and 60 volume percent beryllium. An aluminum coating of 0.00075 to 0.001 inch thickness (18 to 25 μ m) would meet the volume requirement.

Figure 4. Beryllium Wire Before Preplating
(500X)

A plating speed of 10 feet (3 m) per hour was selected for design purposes because it allowed a production rate of 1000 feet (305 m) each 5-day week. Since aluminum plates at about 0.001 inch (25 μm) per hour at the optimum current density of 20 Asf (215 A/m²) the plating zone had to be 10 feet long to yield the desired production rate.

Using these operating conditions, a prototype plating fixture (Figure 6) was designed and constructed. It was made from polypropylene, polymethyl methacrylate, and stainless steel--materials previously found to be compatible with the plating solution¹. In this plater the wire made four back-and-forth passes through the solution. A zone of 2.5 feet (0.76 m) was plated during each pass.

IMMERSION ETCH IN ELECTROPOLISH SOLUTION
(1 MINUTE)

ANODIC ETCH IN PLATING BATH AT 250 ASF
(2690 A/m²)

ELECTROPOLISH (1 MINUTE AT 6 VOLTS)

CHEMICAL POLISH (2 MINUTES)

Figure 5. Four Examples of Preplated Beryllium Wire

Figure 6. Diagram of Prototype Plating Fixture

Each back-and-forth pass zone had its own cathode contact and anode and was powered by a separate rectifier, allowing individual current control. The cathode contact was a small stainless steel rod that rubbed lightly against the wire. A variable speed motor located outside the glove box and connected through a flexible drive shaft to a take-up pulley in the glove box was used to pull the wire through the plating bath.

The fixture was placed in a dry nitrogen atmosphere glove box and filled with plating solution. The plating bath was a diethyl ether solution containing a 3.4-molar concentration of aluminum trichloride and 0.45-molar concentration of lithium aluminum hydride. Plating tests of 0.5- to 2-hour duration were run to determine the maximum wire speed and current density that could be used. The tests indicated that the best plating current density was between 20 and 40 Asf (215 and 430 A/m²) and the maximum wire speed was 12 feet per hour (1 mm/s) (Figure 7). Higher current densities produced discontinuous nodular deposits shown in Figure 8. During these tests periodic reverse current and superimposed ac on dc were evaluated in the first cell to determine if they improved the smoothness of the plate. Both techniques resulted in a slight, but not significant, improvement and were not used during subsequent runs.

Experience with the fixture revealed several problems. The aluminum trichloride in the atmosphere of the glove box attacked the bare beryllium wire causing etching and breaking. This was overcome by enclosing both the plated and bare wire spools in polyethylene bags that were continuously purged with nitrogen. The original design of this fixture did not allow for rinsing the wire after plating and the level-wind wire guide caused wire

SIDE VIEW (300X)

END VIEW (400X)

Figure 7. Side View and End View of Beryllium Wire Plated at 300 Asf (3200 A/m^2)

250 ASF (2690 A/m^2)

150 ASF (1614 A/m^2)

100 ASF (1076 A/m^2)

50 ASF (538 A/m^2)

Figure 8. Nodular Deposits on Beryllium Wire Resulting from High Current Density

breakage as a result of excessive abrasion. These problems were solved by replacing the metal wire guide with a test tube clamp wrapped with a cloth. The plated wire was pulled through the clamp while the cloth was continually saturated with ether under controlled flow from a reservoir. The excess ether dripped into the plating solution. This technique both rinsed the wire after plating and helped make up ether evaporations from the plating solution.

After prove-in was completed, 5000 feet (1524 m) of wire were run in five segments. The fixture was operated continuously but was attended only during 8 hours each day.

After the previous order was completed, a request was received for an additional 500000 feet (152 km) plated with 0.0002 inch (5 μm) of aluminum. Filling this order in a reasonable time required a larger capacity fixture. A figure of 25000 feet (7.6 km) per week was selected as a reasonable production rate. A new fixture (Figures 9 and 10) was designed using these values. This fixture incorporated the modifications made to the original plater and several design changes to improve operation and increase capacity.

Figure 9. Diagram of Production Plating Fixture

Figure 10. Photograph of Production Plating Fixture

In the new design, polyethylene bags covering the spools were replaced with polymethyl methacrylate boxes. Like the bags, they incorporated a nitrogen purge but the wire was more accessible. The bare-wire spool holder was changed so that it would accept the manufacturer's spool. Previously, the bare wire had to be transferred from the manufacturer's spool to a small plastic spool before it was loaded into the fixture. The changes eliminated one operation and increased the length of wire available to the fixture from 1000 feet (305 m) to 40000 feet (12.2 km). The take-up spool was made larger so that it would hold up to 20000 feet (6.1 km) of plated wire.

Also, the plating zone was lengthened 2.5 to 5 feet (0.76 to 1.5 m) for each pass and the reversing pulleys were located at different elevations to allow two passes of wire through a single zone. This increased the plating capacity of the fixture without changing its width. Width of a glove box is important to allow an operator room to thread the fixture. Seven 5-foot (1.5 m) zones were obtained in a fixture as wide as the prototype having four sets of anodes.

The reversing pulleys were made from stainless steel having carbon bushings used as the cathode contacts. This lessened the frictional drag on the wire and, since the pulleys were located further from the plating zone, reduced deposit buildup on the contact. The wire guide on the level wind system was changed from a cloth-wrapped test tube clamp to a carbide pin guide with attached felt pads. This permitted good ether rinsing of the wire after plating and reduced the frictional drag on the wire. Also, the felt pads could be changed more quickly than the cloth. Finally, a tight-fitting, three-piece plating tank cover was added to reduce ether evaporation losses.

A temporary facility using two glove boxes and two plating fixtures was set up so that the order could be filled in less time. During the prove-in of these fixtures it was found that a 0.0002-inch ($5\text{ }\mu\text{m}$) aluminum coating on the uncleaned wire was not continuous, so the Sandia order was changed to a thicker coating of 0.001 inch ($25\text{ }\mu\text{m}$) that was continuous. The best plating current density was still between 20 and 40 Asf ($215\text{ and }430\text{ A/m}^2$), but the wire speed was about four times greater because of the longer plating zone.

Two serious problems were encountered during the early production runs. One problem was improper design of the level winder; the other was excessive wire breakage. The original level winder had a harmonic rather than linear motion causing the plated wire to pile up at the edges of the take-up spool. Such tangling and snarling had not been encountered on the prototype unit because 1000 feet (305 m) of wire did not have sufficient bulk to cause trouble. The problem was corrected by replacing the designed system with an inexpensive fishing reel driven by rubber O-rings. The take-up spools were also changed at this time to match the winding width of the reels. Good level winding was obtained using this system.

The first shipment of bare wire from Sandia had brown Kraft paper between each layer of wire. Earlier material had not been interleaved so no design allowances had been made for this condition. As the wire ran out on one layer, the paper had to be removed to expose the next layer of wire. Wire breakage frequently occurred when the paper was allowed to unreel unattended. Since bare wire will break under tension at about 2.5 pounds (11N) and will fail under shear at much lower values, it was common for the paper to hang up enough to break the wire. This problem was solved initially by aiding the removal of the paper by hand, but the final solution was obtaining wire without interleaves.

After these problems were solved, only an occasional fixture malfunction or a weak spot in the bare wire caused breakage. These new problems were not serious and most of the plated lengths were 5000 feet (1524 m) or more. The fixtures now appear capable of plating 15000 feet (4.6 km) of wire per week while requiring only 10 to 15 man hours of attention. Larger capacity fixtures could be designed if desired.

ACCOMPLISHMENTS

A plating process was developed that allows continuous plating of 0.005-inch diameter (127 μ m) beryllium wire. A total of 505000 feet (154 km) was plated.

Methods of electroplating and CVD coating aluminum on graphite fibers were investigated. All attempts at coating continuous lengths of fibers were unsuccessful.

FUTURE WORK

No future work is planned on this project because at this time there is no application for these composites. A more sophisticated setup would be needed to successfully aluminum plate graphite fibers. This setup must have better process controls, especially improved heating technique, and method of spreading the fibers consistently.

Future work on the beryllium wire depends on the successful application of beryllium-aluminum composites. If this system finds an application, future scaleup to a production operation will be needed.