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NWC

THE USE OF CHEMICAL VAPOR DEPOSITED ALUMINUM FOR PROPELLANT TANK LINERS AND EXPULSION BLADDERS

by

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ABSTRACT. As a part of its liquid propellant positive expulsion program, the Naval Weapons Center (NWC), China Lake, California investigated, on contract, a process for forming a rollonet within a propellant tank after the tank is fully assembled. The process used the chemical vapor deposition (CVD) of aluminum, by thermal decomposition of aluminum alkyl, on the heated interior of the tank walls to form the rollonet. Methods of controlling the adhesion of the deposited aluminum layer to the tank walls were investigated, as were methods of improving alkyl circulation within the tank and techniques to improve the efficiency of the deposition process.

Details of experimental equipment, procedures and processes, and test results are discussed.

Although this brief program did not culminate in the production of a usable rollonet, additional laboratory scale investigation is recommended.

The results of detailed material evaluation conducted by NWC on samples of deposited aluminum supplied by the contractor are presented in photomicrographs, tabulated physical properties data, and X-ray examination photos.

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA * APRIL 1969

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M. R. Etheridge, Capt., USN ..... Commander
Thomas S. Amlie, Ph.D. ..... Technical Director

FOREWORD

This report presents the results of work conducted from November 1966 through September 1967 by Commonwealth Scientific Corp. on contract number N00123-67-C-0311 as a part of Navy in-house support of the AGM-53A Air-to-Surface Guided Missile System (CONDOR) under WepTask RM3731 001/216-1/W107 B0 01.

The Navy in-house CONDOR effort was under the cognizance of the CONDOR Field Activities Program Manager, J. A. Crawford. Thomas Capello was the cognizant Naval Air Systems Command CONDOR Propulsion Engineer.

This report was reviewed for technical accuracy by Leroy Krzycki. Due to the preliminary nature of the work reported, conclusions presented herein are not necessarily final and may be subject to revision.

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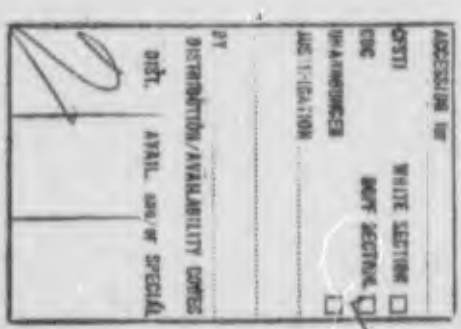

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INTRODUCTION

As a result of a program conducted at Naval Weapons Center (NWC), China Lake, California, to determine the properties of rolling metal bladders (rollonet) for positive expulsion of liquid propellants, interest was generated in the possibility of forming the bladder within the propellant tanks by a plating or deposition technique. The two candidate techniques considered were electroplating and chemical vapor deposition (CVD).

The formation of rolling bladders by electroplating techniques was being investigated by industry[1]; however, CVD feasibility studies had not been initiated. The CVD process has been used during the past several years for a variety of metal coating applications on the exterior surfaces of metal parts and Teflon sheet. No attempt had been made, prior to the work reported here, to coat the inside surfaces of enclosed tanks having only small ports for access to the interior. This requirement stems from the desire to develop a one piece bladder which will contain the propellant and thus decrease the possibility of leakage during long term storage. NWC requested quotations from two companies[2] known to have experience in the CVD process. A small, best efforts contract was awarded to Commonwealth Scientific Corporation for a four-phase program to determine the feasibility of forming rollonets 0.030-inch thick in Government furnished 8-inch diameter 18% Ni maraging steel tanks (Ref. 1).

Phase I of the contract called for a study of methods of controlling the adhesion of the deposited metal to the tank walls. A means of introducing the chemical vapor into the tank interior was to be developed during Phase II. Phase III of the contract called for the determination of deposition variables and their effect upon the quality of a deposited layer of metal. During Phase IV, six tank assemblies were to be processed to form rollonets within their interiors by the CVD process (Fig. 1), assuming that the first three phases of the study were successful. The criteria by which the success of CVD aluminum rollonets were to be judged were ductility, tensile strength, modulus of elasticity, grain size uniformity, impermeability, adhesion of the aluminum to the tank walls, and a successful expulsion.

Mr. D. Frank Bazzarre of Commonwealth Scientific Corporation was responsible for the experimental deposition program.

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[1]TRW Systems Group, Redondo Beach, California

[2]General Technologies Corporation and Commonwealth Scientific Corporation, Alexandria, Virginia.

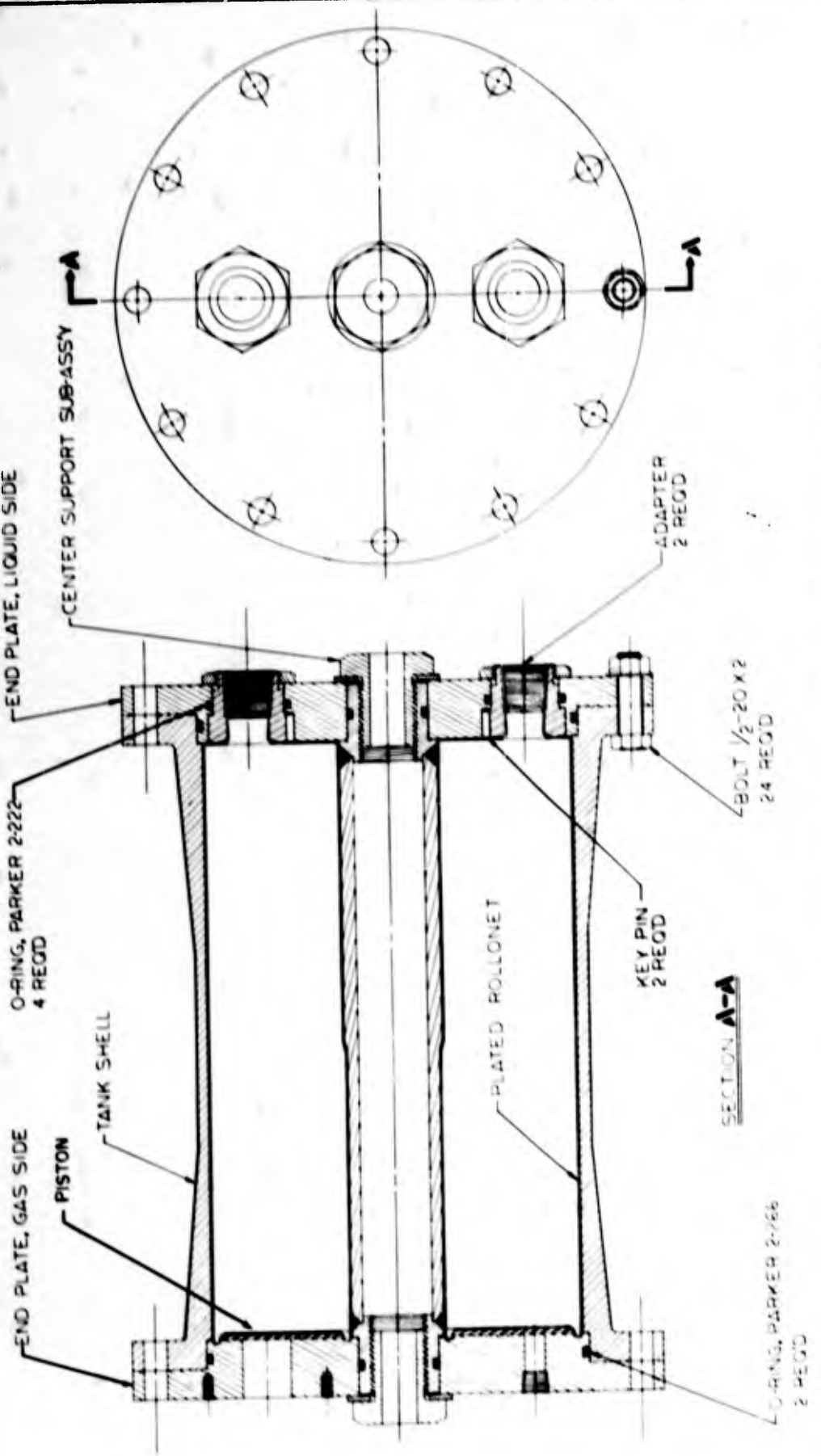


FIG. 1. Tank Assembly for Chemical Vapor Deposited Rollonet.

DISCUSSION

The CVD process utilizes the thermal decomposition of metal alkyl vapors upon contact with a heated object or substrate to be plated. In order for successful deposition to take place, it is necessary that the alkyl be sufficiently unstable so that it can be thermally decomposed to deposit the metal, and be so formulated that self-contaminating by-products will not be produced. Of the aluminum alkyls available, it was determined that ethyl aluminum hydride and triisobutyl aluminum provide the highest quality aluminum deposit. Triisobutyl aluminum was used in this study.

Small maraging steel samples, 1 x 0.125 x 7 inches, were used during Phase I. Initial aluminum deposition attempts were made with half of the sample covered with Teflon tape to provide for easy peeling of part of the deposited aluminum layer to permit grasping. This system did not succeed due to blistering of the Teflon during deposition which in turn prevented a continuous aluminum coating from "bridging" between the tape and steel. Subsequent tests utilized two maraging steel strips that were butted together on a support plate and surface ground to provide a near continuous surface for deposition. For peel testing, the outer end of one strip was lifted away from the support plate and rotated, using the deposited aluminum at the butt joint as a hinge, until it was parallel to the other strip. A measured peeling force was then applied to the 180 degree bend of the aluminum deposited layer, via the steel strips, to test for peel strength.

The system designed in Phase II to plate the interior of the tanks in these experiments (Fig. 2 and 3) included alkyl, suppressant gas, nitrogen carrier gas, supply tanks, a gas distribution system, heat exchanger (vaporizer), gas inlet and outlet manifolds, electric tank heaters, vacuum driven exhausting facilities, and temperature monitoring and control equipment. The design was based on apparatus used in previous programs to coat the exterior of parts by the CVD process. The alkyl liquid, suppressor gas (which controls undesirable side reactions), and the nitrogen carrier gas pass from the supply tanks through flow control valves and into the vaporizer. The gas alkyl vapor mixture is then injected into the 250°C preheated tank interior via the inlet manifold. As the alkyl vapor comes in contact with the tank surfaces it thermally decomposes and plates out an aluminum deposit on the surface. Unreacted alkyl vapor and reaction products are drawn off by the exhaust system which utilizes cold traps to recover some of the unused alkyl. The process is continued until it is anticipated the desired thickness of aluminum has been achieved.

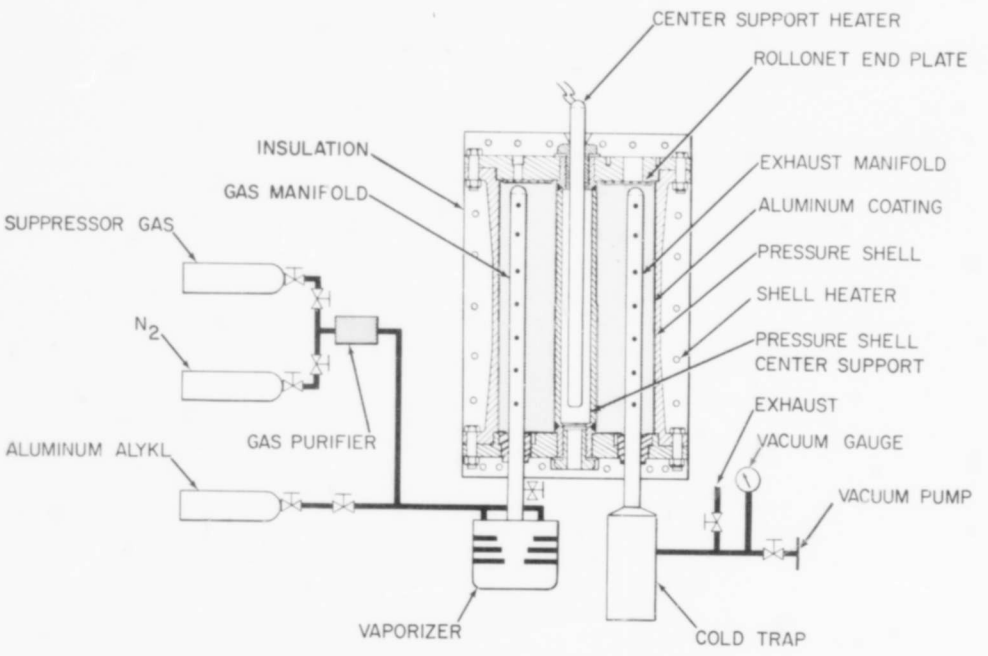


FIG. 2. Schematic Diagram of Plating Set-Up.

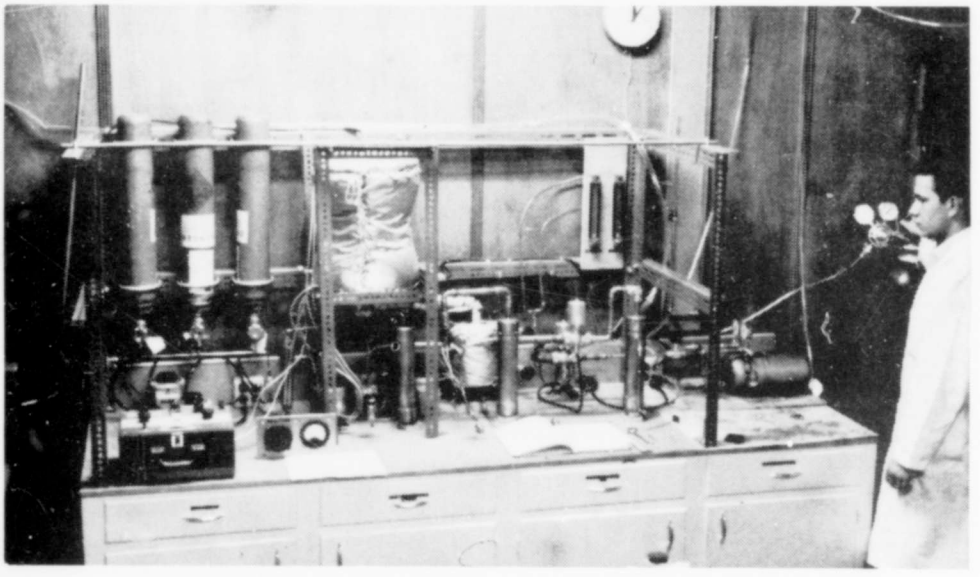


FIG. 3. Laboratory CVD Plating Set-Up.

Phase III of the program investigated the parameters which affect the continuity and quality of an aluminum deposited rollonet. Various methods of alkyl distribution within the tank, to achieve equal deposition thickness, were attempted. Of major interest were hole distribution variations in the inlet and outlet alkyl manifolds and a fan turbulator.

RESULTS

During Phase I, test samples with a 125-microinch surface finish were processed utilizing anodic passivation in 10% sodium hydroxide at 6 volts for periods ranging from 30 seconds to 30 minutes. The results indicated that this process would not yield an adhesive bond between the aluminum and maraging steel with the desired peel strength of 5 to 10 pounds/linear inch. The aluminum coating was keying into recessed areas in such a manner as to tear when attempts were made to peel the coating.

The next approach investigated consisted of chemically cleaning the 18% nickel maraging steel samples to an active surface and heating them in a controlled mixture of argon and air at a ratio of 100:1 for time intervals up to 10 minutes. This process promoted a brown straw colored oxide layer on the substrate surface. The samples were then coated with aluminum. The results were the same as with the chemically oxidized samples.

The general conclusion reached from the investigation of thermal and chemical treatment on the 124-microinch surface-finish maraging steel was that adhesion greater than 20 pounds/linear inch was achieved and that the coating tended to tear instead of peel.

It was therefore necessary to consider other methods for attaining the desired 5 to 10 pound/linear inch aluminum-to-steel peel strength. It was known from previous work that non-uniform surface characteristics were the primary cause of adhesion variation. Therefore, it was decided to investigate surface finish as a method of controlling the bond peel strength. Samples were surface ground to 16-, 32-, and 64-microinch finishes and processed.

The processing of these samples consisted of cleaning with trichloroethylene and acetone. The samples were then coated with aluminum to a thickness of 0.006 to 0.010 inch and peel tested at a 180 degree angle as previously described. The results indicated the 16-microinch finish produced a bond strength with a range of 0.25 to 0.5 pound/linear inch and the 64-microinch samples yielded an average of 3 to 5 pounds/linear inch peel strength.

On the basis of the above tests 10 test specimens having a surface finish of 64 microinches were cleaned, coated with CVD aluminum, and peel tested to determine the peel strength repeatibility. The results indicated that the peel strength varied from 2 pounds/linear inch to 6.75 pounds/linear inch, and averaged 4.2 pounds/linear inch. The coatings were of uniform dull, frosted appearance.

Phase I tests established the plating and sample preparation conditions required to ensure relatively uniform adhesion. Close control of temperature and gas flow rates were necessary to produce a smooth uniform coating. Too high a deposition rate gave a relatively rough surface texture to the coating; too high a plating temperature incorporated carbides into the coating which lowered the tensile strength and varied the adhesive strength during peel.

It was found that surface finish is the most important factor in determining adhesion strength. This parameter is far more important than the chemical or thermal treatment of the surface, provided a uniformly clean substrate surface is obtained. A 64-microinch surface finish was found to be satisfactory. The surface finish of the specimens was verified by an optical comparator to clearly establish this parameter.

Initial Phase III testing of the tank plating system, designed and constructed in Phase II, resulted in a number of problems. These consisted of small leaks in the gas supply lines and the malfunction of one pressure equilization valve. The Buna N seals used on the tank assembly proved unsatisfactory and caused gas leakage to the atmosphere. It was necessary to replace these tank seals with another elastomer, Viton A, which withstood the environment at operating temperatures. While awaiting delivery of a test tank with a 64 microinch internal finish, the first two runs utilized available tanks with 125 microinch internal finish. Each of the tests is described in the following paragraphs, and all tests are summarized in Table 1.

TEST 1

This initial test was primarily a system check-out to establish basic operating parameters for the system and to evaluate overall system performance. The pre-plating cleaning of this unit consisted of a rinse with acetone; no further surface treatment was made to the 125-microinch finish. The duration of this run was 1.5 hours at deposition conditions. Some problems were encountered in holding the deposition temperature within the desired range of 250 ± 5°C for the duration of the run. This was corrected by adding additional voltage controllers to the tank heaters. The coating thickness averaged 0.002 inch and a minimum coating thickness of 0.0012 inch was noted at the joining surface located at the top wall (gas) end of the rollonet. The top (gas) end, at the center support location, appeared to have been exposed to localized higher temperatures

TABLE 1. Summary of CVD Rollonet Deposition Tests Phase III.

Test no.	Surface Preparation	Deposition time (hr)	Average wall temp (°C)	Average deposition thickness (in)	Adhesion lb/linear in	Remarks
1	125μ in. finish acetone wash	1.50	270	0.002	2	Coating was porous and possibly contaminated by aluminum hydride formation
2	125μ in. finish acetone wash	2.42	261	0.003	Poor-blistered	Al_2O_3 initial coating deposit possibly contaminated by aluminum hydride formation
3	64μ in. finish acetone wash	2.50	250	0.003	Poor-blistered	Badly blistered but ductile coating
4	64μ in. finish acetone wash	1.00	253	0.001	2	Al_2O_3 initial coating-test terminated by exhaust line stoppage
5	64μ in. finish acetone wash	5.00	260	0.017	3	Al_2O_3 initial coating-deposit rough and brittle
6	64μ in. finish acetone wash	5.25	254	0.007	5-7	Uniform deposition thickness and texture
7	64μ in. finish acetone wash	22.00	253	0.009	5-7	Fine textured deposit with uneven adhesion failed to expel due to pin holes at joint with installed piston
8	64μ in. finish acetone wash	23.00	251	0.013	1-8	Uniform surface texture - failed to join with piston due to failure of epoxy bond holding piston to tank
9	64μ in. finish acetone wash	11.00	255	0.009	1 up to failure of CVD	Uneven adhesion
10	64μ in. finish acetone wash	4.50	245	0.007	1 1/2 up to failure of CVD	Deposition was terminated due to leak in alkyl vaporizer line
11	64μ in. finish acetone wash	8.75	253	0.017	4 up to failure of CVD	Reaction with epoxy piston-to-tank bond caused brittle CVD deposition - uneven adhesion with some areas impossible to peel

and oxidation (leaking Buna N seal) which resulted in a darkened aluminum deposit. The design of the input and exhaust manifolds was modified in an effort to produce an entirely uniform coating thickness in all areas. The bond strength of the aluminum-to-18% nickel maraging steel tank was 2 pounds/linear inch.

TEST 2

The pre-plating preparation for this 125-microinch surface finish tank consisted of a rinse with acetone. This test was not as successful as Test 1 due to a leak in a supply valve which caused oxidation of the alkyl at run initiation. This formed an initial layer of aluminum oxide and resulted in a non-adherent aluminum coating. The run time was 2.4 hours at full gas flow conditions and resulted in an aluminum thickness of 0.003 inch which appeared to be uniform over all surfaces.

TEST 3

Test 3 was the first conducted with all interior surfaces of the pressure shell ground to a 64-microinch surface finish. A problem was encountered during this run when the Buna N tank seals leaked and caused atmospheric contamination of the system during operation and subsequent oxidation of the aluminum alkyl. The resulting formation of an Al_2O_3 coating on the tank wall caused blistering of the aluminum at the aluminum-to-18% nickle maraging steel interface. The duration of this run was 2.5 hours; an average 0.0025 inch of aluminum was depositied on the interior surfaces of the pressure shell.

TEST 4

Test 4 was severely hampered by operational problems. These problems consisted of alkyl transfer line blockage and exhaust line stoppages. A deposition time of 1 hour was recorded in a time period of 6 hours before it became necessary to stop the run. Subsequent to the run, two problems were noted which contributed to these operational difficulties. The first was leakage of the vacuum exhaust valve, and the second was the leakage of fittings in the exhaust line. These were corrected before Test 5. Viton "A" seals were utilized in Test 4 and performed very well without leakage. The aluminum produced was adherent to the tank walls although there was Al_2O_3 at the aluminum-to-18% nickel maraging steel interface. The coating had a good surface finish and appearance.

TEST 5

Test 5 was a long duration run to attempt the first production of a rollonet. This run was conducted for a period of 5 hours without equipment malfunction. The aluminum thickness varied from 0.005 to 0.019 inches. An Al_2O_3 coating, caused by contaminated alkyl trapped in two valves during the previous test, was again present at the aluminum-to-18% nickel maraging steel interface. The aluminum had a rough surface texture and was brittle, indicating possible carbide and hydride formation. Excessive alkyl was noted in the exhaust products, indicating incomplete decomposition of the gas at the substrate interface. Based on the above results, the following conclusions were reached:

1. To prevent coating contamination, the maximum deposition temperature must not exceed 255°C.

2. The nitrogen flow would be reduced to increase stay time for more complete decomposition of the aluminum alkyl and to reduce directional gas flow which causes uneven deposition.

3. The deposition system would be completely dismantled after each run and thoroughly cleaned to remove all impurities.

TEST 6

Test 6 produced a coating with an average wall thickness of 0.007 inch and an adhesive bond strength of 5 to 7 pounds/linear inch. The duration of the run was 4.5 hours. The deposition system operated satisfactorily with the exception that the vacuum pump malfunctioned after 1 hour of process time. The run was continued and the vacuum pump was repaired and placed back in service after an additional 2 hour time lapse. In general, the deposited aluminum exhibited a uniform surface texture, the wall thickness was uniform, and the bond of the aluminum to the maraging steel pressure shell was satisfactory. It was decided that production of a rollonet with piston for expulsion testing would be attempted during Test 7.

TEST 7

The pressure shell was ground to a 64-microinch surface finish and given an acetone rinse to produce controlled adhesion of the aluminum rollonet to the shell wall. The piston (Fig. 1) was bonded to the gas end plate of the pressure shell at the inner and outer peripheries with a 1/8-inch bead of Duro epoxy; the tank, end plates and center support were then assembled and placed in the aluminum deposition system. Test 7 was conducted utilizing conditions previously determined to be satisfactory for operation. The duration of this run was 22 hours. In

general, the equipment performed satisfactorily with the exception of the solenoid exhaust valves which became saturated with dimerized aluminum alkyl. This resulted in having to stop the vacuum exhaust cycle to prevent pulling air into the system.

Upon attempting expulsion of water with 15 psi nitrogen, pin holes were discovered in the area of the roll preform at the piston inner and outer periphery. The tank was disassembled and the aluminum rollonet examined. The surface exhibited a textured, small crystallite surface, normally associated with good CVD aluminum deposits. The thickness varied from a minimum at one location of 0.008 inch to a maximum of 0.016 inch in another location and with over 90% of the surface having a thickness of 0.013 inch. The bond strength of the rollonet was consistent from 5 to 7 pounds/linear inch. The surface texture and bond adhesion of the rollonet to the pressure shell were believed to be satisfactory.

TEST 8

Deposition in Test 8 was maintained for a period of 20 hours. The average wall thickness of the rollonet was 0.013 inch with an average peel strength of 5 pounds/linear inch. The differential thermal expansion between the aluminum piston and the stainless steel tank end resulted in the epoxy adhesive shearing at their interface. This resulted in the rollonet not plating onto the piston periphery. The aluminum exhibited a uniform surface structure.

TEST 9

Test 9 run time was 10.5 hours. This run was terminated early due to stoppages in the exhaust line of the deposition system. To prevent the thermal expansion shear of the epoxy joint at the piston to tank-end interface, a wider bead of epoxy (approximately 3/16 inch) was used for the seal. This seal performed satisfactorily during the deposition process. The average wall thickness of the CVD aluminum was 0.009 inches. The aluminum deposition at the piston to gas end plate joint was insufficient and leaked when tested to 30 psi nitrogen pressure. Unsuccessful attempts were made to fill the leaks with epoxy. At this point, mechanical expulsion was investigated by applying mechanical force through the two ports in the gas pressure end plate. The piston deformed inward approximately 0.375 inch and ripped away from the inner and outer deposited diaphragms.

TEST 10

For Test 10, a new high temperature epoxy was used on the piston. The unit was processed for 4.5 hours before a leak in the alkyl vaporizer forced an immediate termination of the run. This leakage was caused by a rupture in one line on the vaporizer. The unit was evaluated and found to have an average wall thickness of 0.007 inch and a peel strength of 4 pounds/linear inch.

TEST 11

The unit was processed for 8.75 hours, utilizing 10 pounds of aluminum alkyl. The run was terminated early due to a stoppage in the exhaust line. This run was conducted to investigate reaction of the epoxy seal with aluminum alkyl. The average coating thickness was 0.017 inch, and the average peel strength 4 to 5 pounds/linear inch. Definite evidence of a detrimental reaction between the epoxy and the reactant gases at the interface of the piston and the tank gas end plate was observed. This reaction caused deterioration of the aluminum coating and prevented successful operation of the rollonet. In subsequent tests, it was decided to apply epoxy only to selected areas to provide sufficient adhesion to hold the piston in position during deposition.

Due to limited funding, Test 11 was the final CVD rollonet attempt under Phase III. Using redirected Phase IV funding, seven additional attempts to produce usable rollonets resulted in basically the same difficulties previously encountered in Phase III. Each of the first four tests investigated a variation in the alkyl inlet and outlet flow patterns. This was accomplished by selectively masking off sections of the hole patterns in the inlet and outlet manifolds. Each of the four rollonets leaked upon pressuriation and were of insufficient thickness (0.020 inch maximum). It was concluded that the manifold variations did not succeed in providing uniform distribution of the alkyl. During Tests 5 and 6 of Phase IV, the tank was inverted 180 degrees to cause the dense alkyl vapor to settle in the piston end of the tank. The purpose was to attain maximum aluminum thickness in the area of the CVD aluminum joint to the piston. The coating did attain a thickness of 0.028 inch, but was brittle due to retention of reaction products in stagnant areas.

In the final attempt to form a rollonet by the CVD process, a turbulating fan mounted in the liquid end plate of the tank was utilized. The fan provided sufficient circulation of the alkyl to allow deposition of aluminum 0.010- to 0.013-inch-thick, on all surfaces of the tank. This 0.003-inch difference in thickness would be acceptable if the full 0.030-inch-thick deposit had been attained. The CVD aluminum was ductile but was covered with lumps, possible due to alkyl buildup on the fan being thrown against the tank wall. Phase IV results are summarized in Table 2. Figure 4 illustrates the interior of a tank assembly after CVD coating.

TABLE 2. Summary of CVD Rollonet Deposition Tests Phase IV.

Test no	Manifold configuration		Deposition time, hr	Av. wall temp, °C	Av. deposition thickness, in	Adhesion lb/linear in	Remarks
	Inlet	Exhaust					
1	Middle 5 in and top 2 in open	Middle 4 in and top 1 in	9.50	256	0.009	1-8	Uniform coating, but failed to join to piston.
2	Bottom 1 in and top 1 in open	Bottom 1 in top 1 in open	9.0	251	0.011	1-4	Insufficient joining to piston to allow expulsion. Coating on center support would not peel.
3	Cut off to 2 in length	Same as test no. 2	5.50	250	.....	Greater than CVD shear strength	Very poor coating which could not be peeled.
4	Top 2 in open	Bottom 2 in and top 2 in open	9.0 over 2 day period	254	0.015	4 up to failure of CVD	Brittle, laminated coating which could not be peeled from center support.
5	Full length open. Tank inverted	Full length open	9.0	255	0.010	4	Inversion of tank caused thicker coating to be formed at piston end, but was insufficient to allow expulsion.
6	Same as test no. 5	Same as test no. 5	11.0	246	0.009	1-4	Same as No. 5.
7	Same as test no. 5	Same as test no. 5	15.0	254	0.012	1	Same as No. 5.

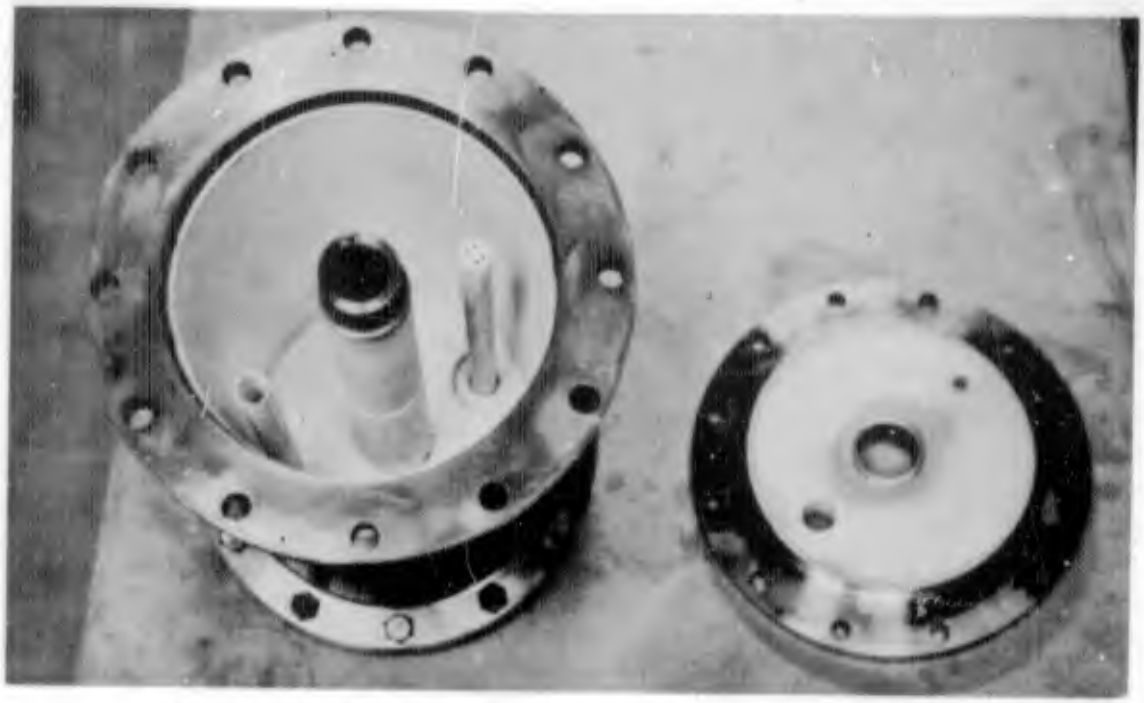


FIG. 4. Tank Assembly with Interior CVD Coated.

Samples of CVD aluminum from various runs in Phase III and Phase IV were sent to NWC for metallographic study. A discussion of the results of these studies follow.

MATERIAL PROPERTIES OF CVD ALUMINUM

As part of the evaluation of vapor deposited aluminum, a study was made of the metallurgical properties of representative samples. Physical and chemical properties were investigated to see how they compared with those of 1100-0 mill rolled aluminum sheet. The microscopic structure of samples obtained from four deposition trails was investigated with the aid of a scanning electron microscope. Reference 2 is a comprehensive treatise on the theory and operation of the stereoscan electron microscope. Figure 5 through 8 show the samples A, B, C, and D at four different magnifications, each figure shows the four samples at a given magnification so that they can be compared. Samples A, B, and C are the structure of the free surface while sample D is of a surface next to the substrate. A leak developed in the system during the deposition of sample C accounting for the frothy appearing substance in this specimen which is either aluminum oxide or some other dielectric. Any non-conductive substance which is viewed with the scanning electron microscope builds up a charge which gives a washed out appearance to that substance. Note the single crystal in the center of the photograph. It is probably aluminum since it appears to be conductive and all envirioned contaminants would be non-metallics.

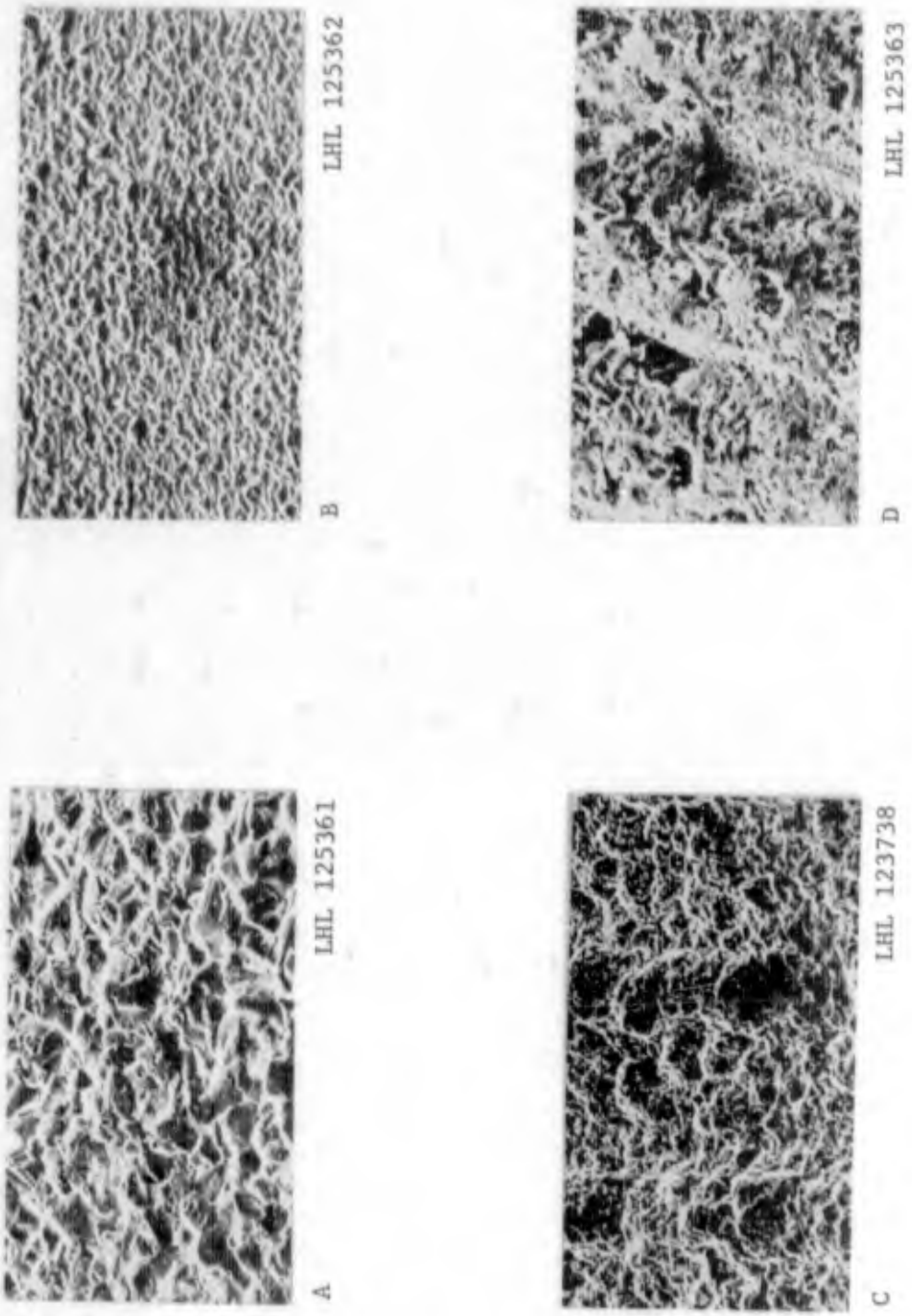


FIG. 5. CVD Aluminum Surface Structure of Four Samples at 200 X.

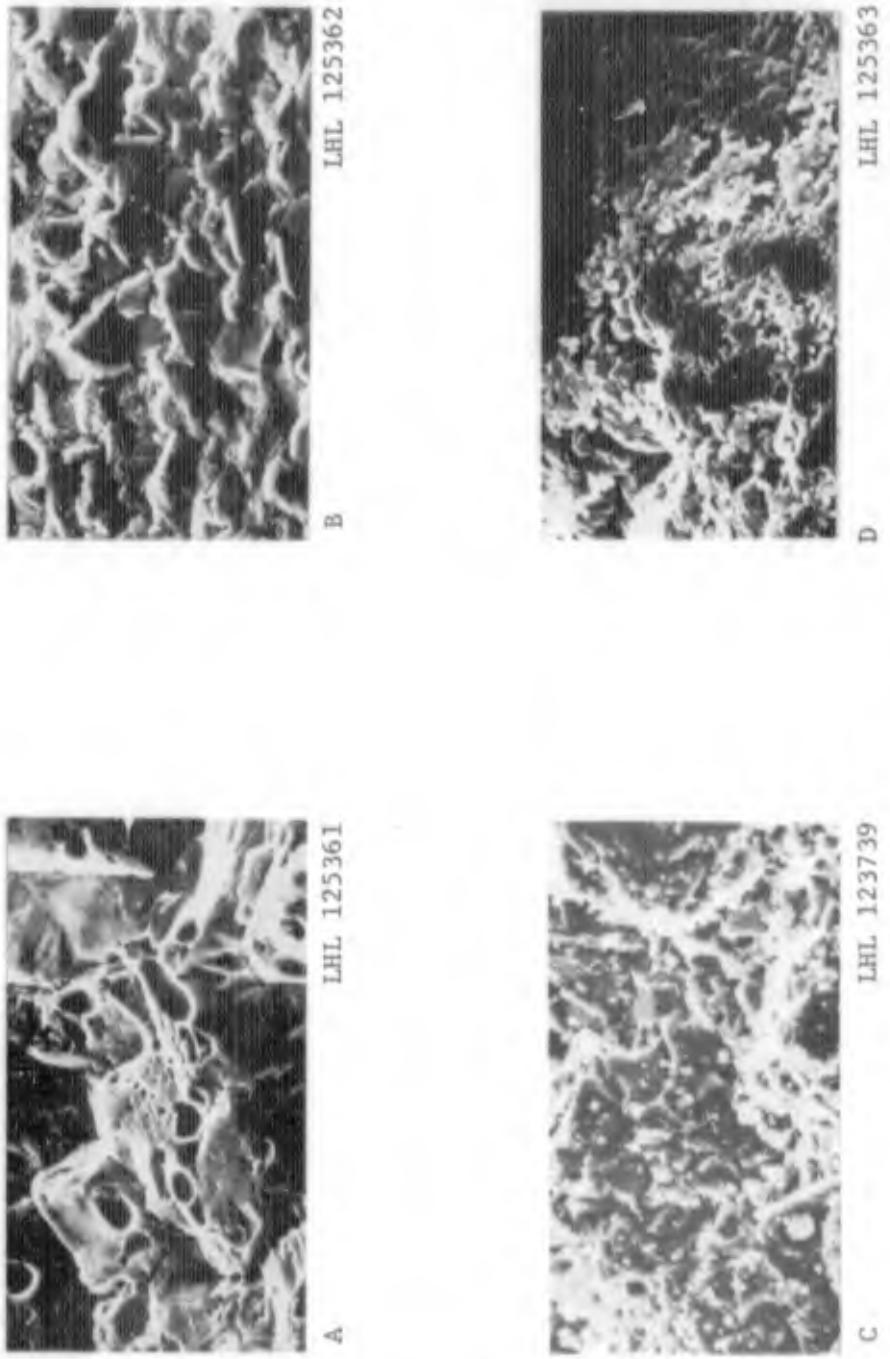
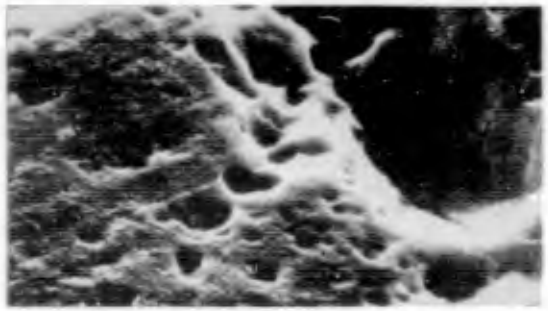


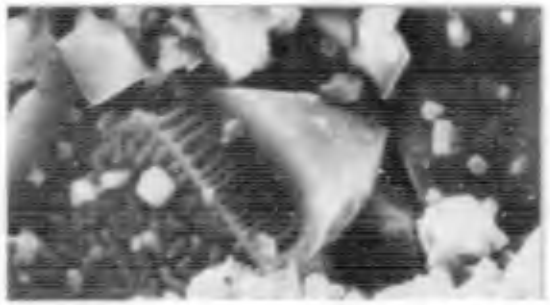
FIG. 6. CVD Aluminum Surface Structure of Four Samples at 1000 X.

FIG. 7. CVD Aluminum Surface Structure of Four Samples at 2000 X.

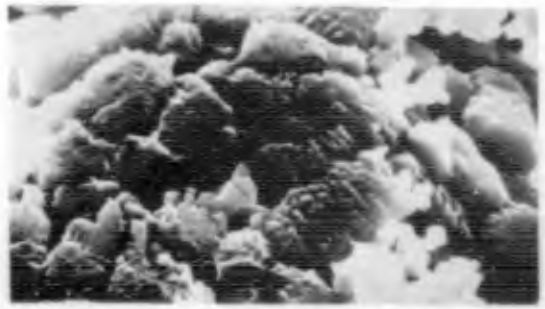


A LHL 125361

B LHL 125362



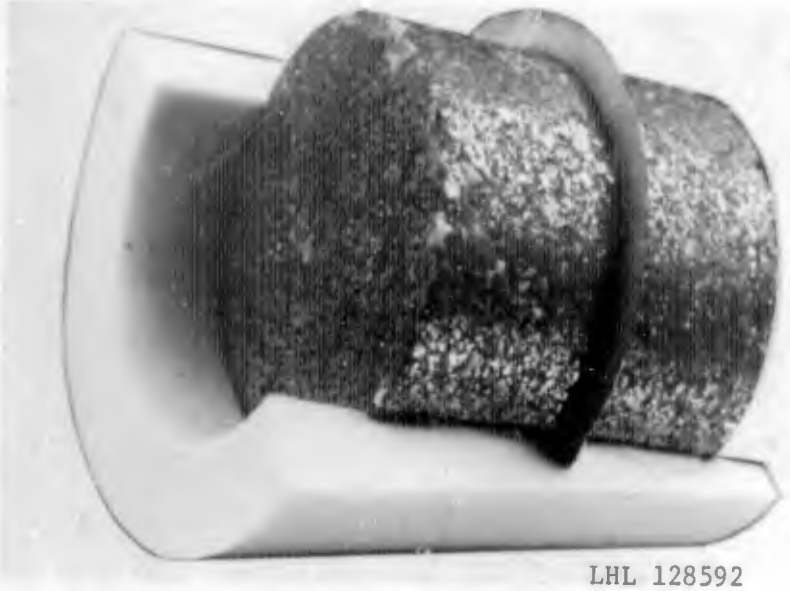
C LHL 123739



D LHL 125364

FIG. 8. CVD Aluminum Surface Structure of Four Samples at 5000 X.

Permeability of the CVD aluminum was of prime concern since the aluminum was being developed for long term propellant storage. Samples 0.014 and 0.003 inch in thickness were mounted between two cylinders of porous sintered nickel and then potted in a tapered cylinder using silicone rubber (Fig. 9). This assembly was pressurized with argon to 100 psi; the gas flow to be measured by a water displacement technique. Neither thickness of material showed gas passage during a 60-minute pressurization cycle.



LHL 128592

FIG. 9. Permeability Sample at 5 X.

Tensile tests were run on two samples which were cut from 0.014-inch-thick CVD aluminum. The following results are trends only since more tests would be needed to determine material properties within a specified confidence limit. The second sample broke through a gage mark and is therefore subject to question.

Sample No.	Ultimate Stress	Elongation[a]	Modulus
1	5714 psi	5.5%	0.336×10^6
2	5144 psi	4.0%	0.235×10^6

[a]Elongation obtained from gage marks on specimen before and after testing.

The low stress and modulus values obtained from these tests can be attributed to inhomogeniety caused by voids and/or inclusions. To help in ascertaining the reason for the poor physical properties, the fracture surface was cut from one of the above tensile specimens and then examined with the aid of a stereoscan electron microscope. Figure 10 depicts this

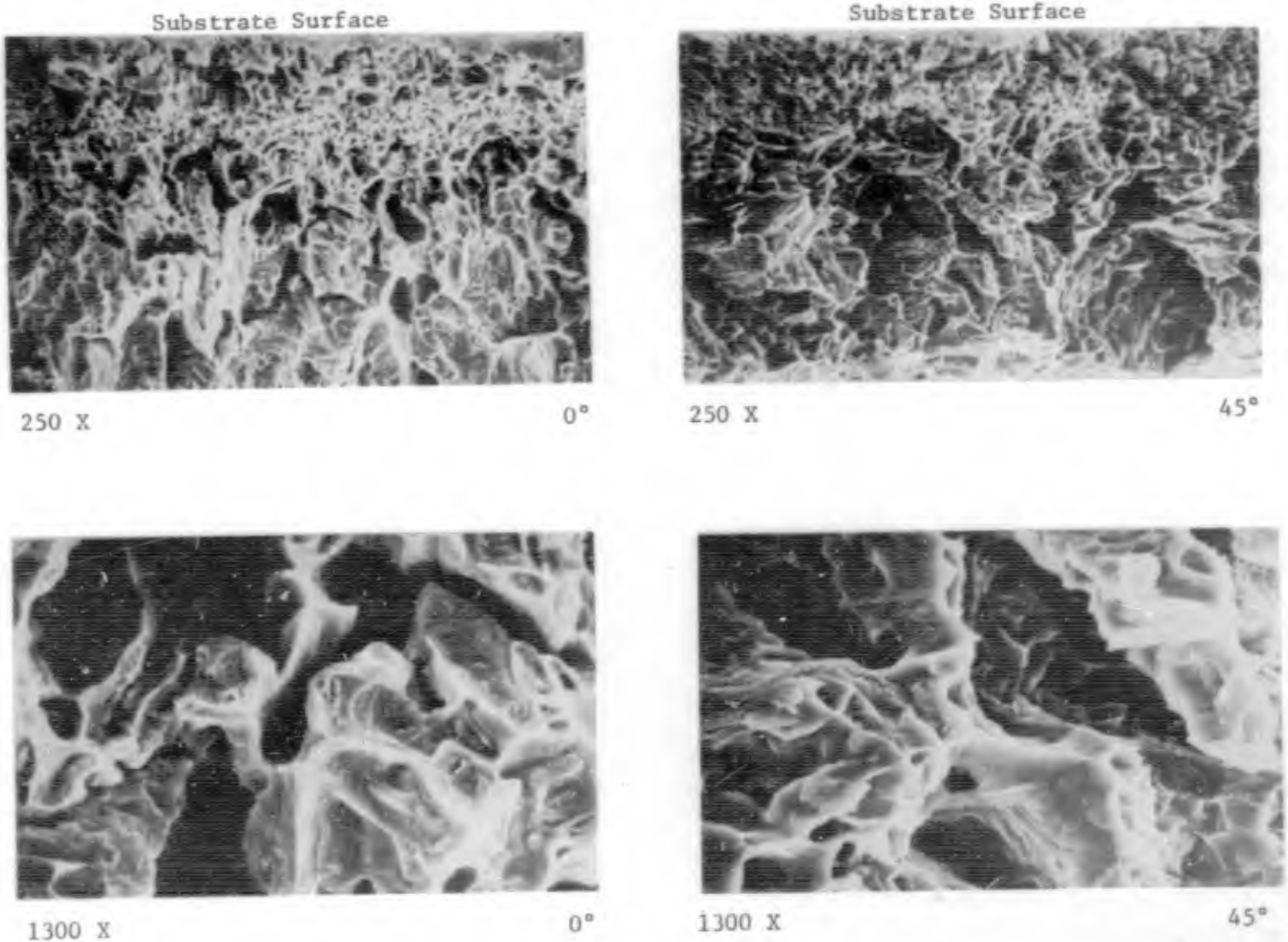


FIG. 10. Fracture Surface.

sample at two different magnifications. Two of the views are looking normal to the specimen (0 degree inclination) while the second two views are looking into the specimen at a 45 degree angle. It can be seen that the first aluminum to deposit on the substrate is of much finer grain size than that which deposited later. Voids in the material can be clearly seen although it is not possible to obtain a quantitative measure of the size and quantity of voids.

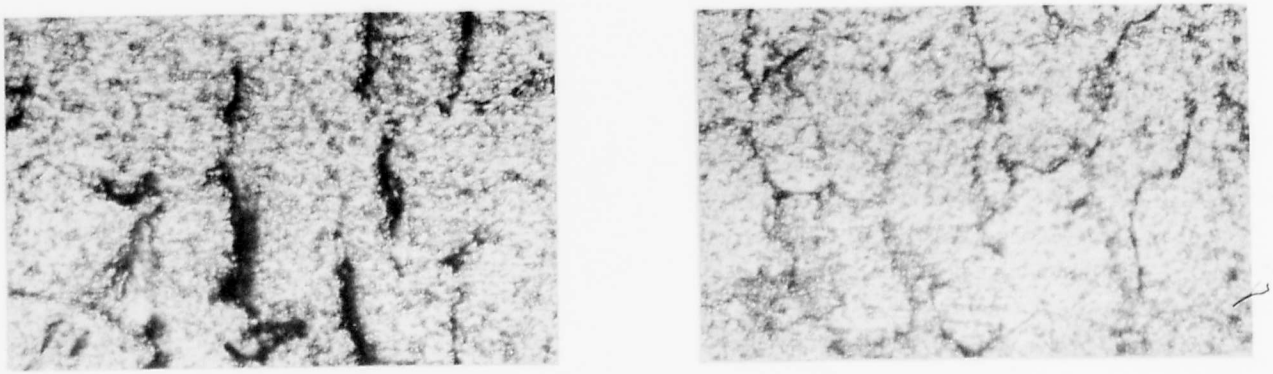
Specific gravity determinations showed a range of 2.38 to 2.50 compared to the accepted value for aluminum of 2.70. An X-ray diffraction pattern of a sample showed the material to be primarily aluminum, together with a small amount of material which could not be identified. The pattern also indicated the presence of some fairly large crystals of aluminum. The X-ray absorption of a sample was compared to various thicknesses of aluminum (stacked foil). The absorptivity of the sample was found to be 22.7% less than that of an equivalent thickness of aluminum foil. To determine if this finding was due to the presence of low atomic number elements such as hydrogen and carbon, the sample was analyzed for these constituents; the results showed less than 0.05 parts per million.

Figure 11 shows two views of a polished and etched cross section. The third view is a microradiograph representing the condition of the sample near the surface away from the wall on which the deposition was made. Note the large size of some of the grains and the dark areas at some of the grain boundaries.

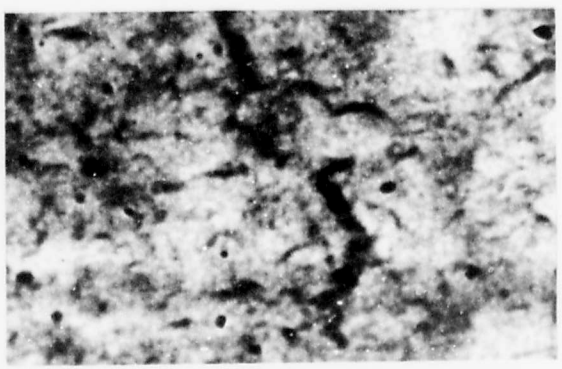
The material studies show that voids are present in the CVD aluminum. The X-ray diffraction gives indication of an element which has not yet been identified. This element, in addition to the voids, could be contributing to the low density and other physical properties of the CVD aluminum.

SUMMARY AND CONCLUSIONS

The initial studies on surface preparation of the tank walls, to achieve the desired bond peel strength of 5-10 pound/inch, indicated that techniques such as anodic passivation in 10% sodium hydroxide or acid etching did not provide reliable and reproducible peel strengths. It was determined that surface finish was the controlling factor in obtaining reproducible peel strengths. Experiments indicated that a 16-microinch finish produced bond peel strengths with a range of 0.25 to 0.5 pound/linear inch, 32 microinch produced a range of 0.5 to 2.5 pound/linear inch, 64 microinch yielded 3 to 5 pound/linear inch and 125 microinch resulted in 20 pound/linear inch or greater. The interiors of the test tanks were surface ground to a 64-microinch finish for subsequent plating experiments.



Polished and Etched Specimen at 500 X.



X-ray Absorption Pattern at 140 X.

FIG. 11.

Difficulties were encountered during experiments aimed at producing CVD rollonets suitable for expulsion testing. The basic problems encountered were insufficient CVD aluminum thickness (poor decomposition efficiency), and variations in metallurgical properties and non-uniform deposit causing poor joining to the pre-installed piston. These difficulties were primarily the result of insufficient gas flow to create turbulent flow within the closed tank and attempts were made to artifically turbulate the flow by means of manifold variations and an internal fan. None of these significantly improved the quality of the deposited aluminum or the ability to achieve the full 0.030 inch thickness. As a result, no usable rollonets were forthcoming from this program.

The results of this program have demonstrated that many of the parameters which affect the deposition of a high quality CVD aluminum rollonet are unknown. In order to fully determine the feasibility of using the CVD process for fabrication of expulsion bladders or tank linings, a study is necessary to determine the effects of various parameters. Because of cost, such a program should be carried out using laboratory tanks smaller than those used in this study in order for the maximum number of data points to be obtained.

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13. ABSTRACT

As a part of ~~its~~ a liquid propellant positive expulsion program, the Naval Weapons Center (NWC), China Lake, California investigated, on contract, a process for forming a rollonet within a propellant tank after the tank is fully assembled. The process used the chemical vapor deposition (~~CVD~~) of aluminum, by thermal decomposition of aluminum alkyl, on the heated interior of the tank walls to form the rollonet. Methods of controlling the adhesion of the deposited aluminum layer to the tank walls were investigated, as were methods of improving alkyl circulation within the tank and techniques to improve the efficiency of the deposition process. Details of experimental equipment, procedures and processes, and test results are discussed.

Although this brief program did not culminate in the production of a usable rollonet, additional laboratory scale investigation is recommended.

The results of detailed material evaluation ~~conducted by NWC~~ on samples of deposited aluminum ~~supplied by the contractor~~ are presented in photomicrographs, tabulated physical properties data, and X-ray examination photos.

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