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FABRICATION OF BERYLLIUM - VOL. IV
SURFACE TREATMENTS FOR BERYLLIUM ALLOYS

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ABSTRACT

This report documents the surface treatment techniques developed for use in the fabrication of beryllium aerospace vehicle structures. It is Volume IV of a six volume set of technical reports entitled "The Fabrication of Beryllium." Proven techniques for the removal of surface contaminants resulting from in-process shop handling, and specific pre-cleaning and activation procedures for the preparation of the surface for subsequent operations such as plating and brazing, are reported.

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

[redacted]

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Mr. R. F. Williams, NASA Advanced Manufacturing Programs, was the Project Manager of this effort under the management of Mr. A. J. Steele, Manager, NASA Engineering Programs, Lockheed Missiles and Space Company. The work was performed under the technical direction of Mr. S. E. Ingels, assisted by Mr. C. Fruth in preparation of the final report.

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The other Volumes of Technical Memorandum X-53453 are:

Vol. I. A Survey of Current Technology

Vol. II. Forming Techniques for Beryllium Alloys

Vol. III. Metal Removal Techniques for Beryllium Alloys

Vol. V. Thermal Treatments for Beryllium Alloys

Vol. VI. Joining Techniques for Beryllium Alloys

MANUFACTURING ENGINEERING LABORATORY

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SECTION I. INTRODUCTION

The objectives of this task are the development and documentation of the beryllium fabrication operations classified as "Surface Treatment" in the Beryllium Fabrication Methods Development Program Plan.

Maximum use was made of the established methods and procedures currently being utilized in production operations. In all cases, the verification and recording of pertinent data was necessary; in many cases, e.g., precleaning methods for subsequent brazing or plating, additional development work was required.

The procedure used in compiling this report was as follows:

1. Conduct an analysis of the surface treatment practices being used within industry.

2. Investigate, evaluate, and report upon the techniques currently utilized.

3. Conduct additional development work in those areas lacking definitive procedures.

SECTION II. GENERAL CLEANING

The selection of a suitable process for the cleaning of beryllium is largely dependent upon the nature of the subsequent process or operation, i.e., the processes used for the general cleaning of detail parts may not be suitable for the preparation of the surface for adhesive bonding, brazing, or the final cleaning of assembled structures.

Therefore, only those procedures suitable for the removal of surface contaminants such as fingerprints, lubricants, dust, fine metal particles, etc., resulting from in-process shop handling and processing are discussed in this section. Specific procedures for cleaning the surface during preparations for subsequent operations are discussed separately under appropriate headings.

As required during the fabrication of beryllium parts, the surfaces should be solvent-wiped with lint-free cloth, or "Kimwipes," and methyl ethyl ketone (MEK). This routine production procedure readily and successfully serves for the removal of lubricants, DYKEM (bluing compound commonly used for layout purposes), and other contaminants including superficial fingerprints. If the fingerprints are lightly etched into the material, scrubbing with a fine abrasive such as "unchlorinated Bon Ami," followed by wiping with MEK, may be necessary to remove this contamination. Deeply etched fingerprints, the heavy oxide film formed during "hot forming" operations, or other gross contaminants must be removed completely to provide a uniform surface for subsequent operations. This cleaning operation is most satisfactorily accomplished by wet sanding to provide a metallographically uniform surface, followed by light etching (0.0005 to 0.001 inch per surface) in a solution of sulfuric acid, nitric/hydrofluoric acid, or ammonium bifluoride. The light oxide film, normally existing on the surface of the material, may be successfully removed by light etching only and the wet sanding operation is not required.

Satisfactory production cleaning procedures, therefore, can be outlined as follows:

1. Remove the lubricants, dust and similar surface contaminants by wiping with MEK.

2. As necessary, sand with 180, or finer, grit "Screenback Metallic Coated Abrasive-Doubler Flex" cloth (Aluminum Oxide, available from the Behr-Manning Company, Troy, N. Y.).

3. During the sanding operation, flood the part continuously with water. The part must be kept wet at all times during this operation.
   WARNING: The sanding must be accomplished within a protective enclosure and the abrasive cloth must be disposed of in approved containers to prevent the airborne distribution of finely dispersed particles as the cloths become dry.

4. Wipe the parts with MEK.

5. If required, etch lightly.

6. Rinse the parts in clear water and oven-dry at a temperature of 180-200°F for 30 minutes to remove all moisture.

7. Wrap the parts in neutral protective paper.
   NOTE: The cleaned parts shall be handled only with clean dry gloves.

During an extended period of time many alternate methods for the general cleaning of beryllium have been investigated; including immersing the parts in acetone, trichloroethylene vapor, and several proprietary compounds; solvent wiping with methyl chloroform; and anodic cleaning.

Although several of these methods were satisfactory, none appeared to be superior to the simple straightforward procedure previously outlined, and several presented serious problems due either to the lack of compatibility with subsequent operations, or the entrapment of cleaning fluids in the pores of the material or between the faying surfaces of assemblies.

The results of the tests conducted to investigate and evaluate the cleaning efficiency of hot solutions of several proprietary compounds are presented in Table I. All of the solutions were maintained at a temperature of 190°F and, except as noted, all of the beryllium samples were immersed in the solutions for 10 minutes.

TABLE I

CLEANING EFFICIENCY

COMMON PROPRIETARY COMPOUNDS

Cleaner	Surface Attack	Soil Removal	Remarks
Con-0-69	Slight darkening	Fair	Some surface residue after 5 minutes
Oakite 161	None	Slight residue	
Kelite 263	Some roughing	Good	
Alkalume 13	None	Good	Note slight attack after 1/2 hour
Altrex	None	Good	

It is recognized that this investigation was not all inclusive, and that other production cleaning methods are being utilized routinely within the industry.

SECTION III. SURFACE PREPARATION AND TREATMENT

A. GENERAL

Beryllium is self-passivating through the almost immediate formation of an extremely thin surface layer of beryllium oxide upon the exposure of the surface to normal atmosphere. Although this characteristic is desirable in that it prevents the continued oxidation of the material, the beryllium oxide also inhibits the proper accomplishment of certain subsequent operations. Appropriate means, therefore, must be employed for the removal of this oxide layer and the temporary prevention of its recurrence. The type of subsequent surface treatment to be applied must be considered to insure the selection of a compatible process. For example, the process used to prepare the surface for adhesive bonding is quite different from that used to prepare the surface for plating.

The various specific cleaning processes, therefore, are discussed separately under appropriate headings.

B. BONDING

The cleaning materials and techniques used during the preparation of the surface for bonding must be compatible with the bonding agent to be used. If incompatible, minute traces of the cleaning agent in the surface of the material may vaporize, or out-gas, during high temperature curing cycles and inhibit the proper curing of the bonding material. Although every precaution is taken to insure the removal of all residue, the possibility of microscopic entrapment in the pores of the beryllium must be considered. Therefore, the utilization of a "neutral" or "bond compatible" cleaning process is indicated.

The information and data contained in various reports and memoranda, the procedures utilized elsewhere, and the processes currently being utilized for one particular production operation were considered. The procedure found to be most suitable for the cleaning of beryllium in preparation for bonding is detailed as follows:

1. Vapor degrease in trichloroethylene vapor
   NOTE: Parts or assemblies which may entrap contaminants and which cannot be effectively flushed or solvent-rinsed throughout, or contain plastic or oil impregnated bearings, or are painted, shall not be processed by vapor degreasing.

2. Immerse the parts for three minutes in a 20 percent (by weight) solution of sodium hydroxide and water at a controlled temperature of 180 ± 5°F.
   NOTE: A 7.5 percent (by weight) solution of "Prebond 700" (Bloomingdale Department, American Cyanamid Company, Havre de Grace, Maryland) and water at a controlled temperature of 200 ± 5°F for ten minutes also may be used.

3. Remove the part from the cleaning solution tank and wash in de-ionized water.

4. Remove the part from the rinse tank. If "water break" occurs, repeat the entire cleaning procedure.

5. Dry the part in a forced-air drying oven, equipped with air filters, at a controlled temperature of 290 ± 5°F for 30 ± 5 minutes.
   NOTE: Hot forced dry air, outside an oven, may be used if no oven is available, providing suitable precautions are observed to avoid recontamination of the part. The cleaned parts shall be handled only with clean dry gloves.

In order to avoid recontamination of the cleaned beryllium parts, it is suggested that the bonding operation be initiated immediately after the completion of the cleaning process. The careful observance of all of the steps in this procedure has resulted in the consistent production of good bonds. The actual bonding procedure may be found in the "Joining" portion of the final report of the Beryllium Fabrication Methods Development Program.

C. PLATING

The quality and integrity of the plating is largely dependent upon the initial condition of the surface of the material to be plated. Because of the sintered powder form of the material, minute traces of contaminants or cleaning solutions may tend to remain in sharp surface depressions or in the pores of the material.

As stated on page 2 of this report, the normal light oxide film and other residual surface contaminants may be successfully removed by light etching. A solution consisting of 45-50 percent nitric acid, plus 1-3 percent hydrofluoric acid, plus water at a controlled temperature of 90 ± 5°F for a period of 1-2 minutes produced a satisfactorily etched surface. The slight roughness of this surface, visible in Figure 1, provides a good bonding interface for the subsequent plating operations.

The surface of the beryllium then was activated for plating by the deposition of a thin copper film or "strike" subsequent to treatment in a zincing solution; the composition of the zincing solution was as follows:

$Zn0$	100 grams
$Na0H$	500 grams
$FeCl_3.6H_20$	100 grams
$NaKC_4H_40_6.4H_20$	10 grams
$NaN0_3$	10 grams
H_20	To make one liter

The processing parameters for this zinc activation treatment were as follows:

Specific Gravity	39-46° Be
Temperature	115-125° F
Agitation	Mild 10-20 FPM
Immersion Time	6-9 Seconds

"Rinse thoroughly in de-ionized water and transfer immediately WITHOUT DRYING."

The activated beryllium then was transferred into a cyanide copper strike solution consisting of:

Dupont Elchem 1469	50 gm/liter
NaF	20 gm/liter
$NaC0_3$	45 gm/liter
$NaKC_4H_40_6 \cdot 4H_20$	20 gm/liter

This operation was conducted at a temperature of 135°F, adjusted with KOH to a pH of 10.5, with a current density of 50-150 asf, for one minute. The appearance of the surface after this activation treatment was a uniform matte pink.

The activated beryllium then was transferred into the following copper pyrophosphate plating solution:

$Cu_2P_20_7$	65 gm/liter
$K_4P_20_7 \cdot 3H_20$	260 gm/liter
KOH	As required to obtain desired pH

NH_4OH	6 gm/liter
*PC-1	250 cc/liter

During the plating operation, the solution was maintained at a temperature of 135°F and a pH of 8.3. The plating operation was continued at a deposition rate of 0.0015 inch per hour until the desired thickness of copper had been deposited. Figure 1 presents a cross-section of this copper-plated beryllium surface.

The nickel plating of beryllium was accomplished by using either of two alternate methods. The first was identical with the previously discussed copper plating procedure, except that the nickel plating operation replaced the final copper plating step. Following the application of the copper "strike," the activated beryllium was transferred immediately into the following nickel plating solution:

$NiSO_4 \cdot 7H_2O$	300 gm/liter
$NiCl_2 \cdot 6H_2O$	35 gm/liter
H_3BO_4	43 gm/liter
†WA7	1 gm/liter

The solution was maintained at a temperature of 120°F and a pH of 3.2; the plating operation was continued until the desired thickness of nickel had been deposited. Figure 2 presents a cross-section of this nickel-plated beryllium surface after it had been subjected to fracture (peel) testing.

The alternate procedure was to transfer the zinc-activated beryllium immediately into the nickel plating solution -- omitting the copper strike step. A good plate was obtained, but additional work will be required to fully evaluate the results.

*Proprietary leveling agent.

†Proprietary wetting agent.

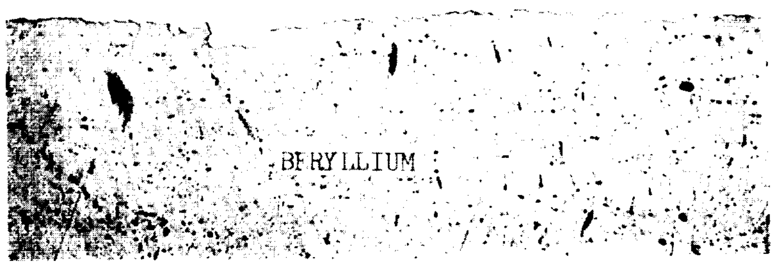
During the laboratory scale development work, the zinc activation copper strike process has been found to be quite reliable. During the peel tests conducted at room temperature, particles of beryllium separated from the parent metal and remained adhered to the copper plate; the failure was in the parent beryllium metal, not in the plating. This condition is clearly visible in Figure 2.

It should be emphasized that, although the above processes did indeed result in the production of satisfactory plating, their total reliability has not yet been established in production operations. In addition, the use of plating as the substrate for subsequent brazing, reported in the "Joining" portion of the study, also has not yet progressed beyond the laboratory stage. Therefore further work is recommended.

D. HANDLING PRECAUTIONS - PROTECTIVE COATINGS

Because of its sintered powder composition, the lack of adequate slip planes at ambient temperature, and an extremely high modulus of elasticity, beryllium is considered to be one of the more brittle materials. In addition, beryllium is highly notch sensitive. It is mandatory, therefore, that suitable precautions be observed during handling, processing, and transportation to avoid damage to the material. Storage shelves and transportation and handling devices must be free of protruding nails, chips, etc., and should be lined with felt or similar protective material. Raw material storage racks should be designed to prevent foreign objects from falling on, or striking against, the material. Chemically inert protective wrapping paper (Mil-P-17667, or equivalent) should be interleaved between the sheets to prevent scratches, abrasions, and nicks. Block material, or small pieces, may be more conveniently protected by wrapping in the protective paper or by storing in individual lined containers.

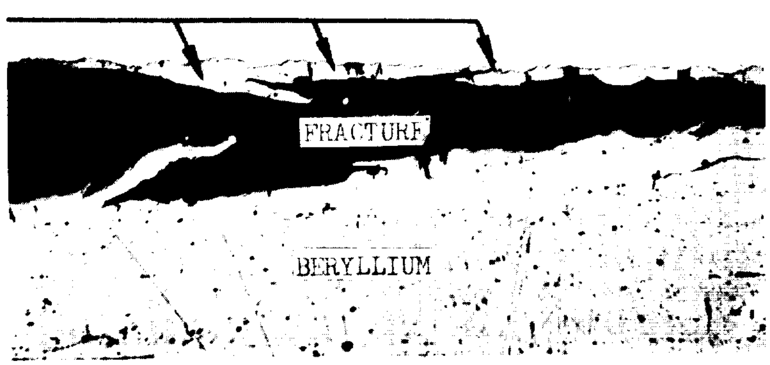
COPPER



BRIGHT FIELD AS POLISHED 500X

FIGURE 1. COPPER-PLATED BERYLLIUM SURFACE

NICKEL



BRIGHT FIELD AS POLISHED 500X

FIGURE 2. NICKEL-PLATED BERYLLIUM SURFACE FRACTURE TEST AT BOND INTERFACE

Plasticized vinyl coatings, such as TEC-704 or TYGON TP-81, may be used as an alternate protective covering. These hand-strippable coatings are easily removed prior to initiation of manufacturing operations.

With the exception of surface plates, and tooling and gaging bases, the tops of work benches and other work surfaces should be covered with a layer of felt, expanded polyethylene, or similar material to avoid damaging work in process. The surfaces of work in process can best be protected by storing temporarily in individual lined containers, or by nesting identical parts with interleaves of protective paper.

Completed parts should be handled only with clean, dry plastic or cotton gloves to avoid fingerprint contamination, and then should be individually wrapped in chemically inert protective paper prior to shelf or container storage, or packaging for shipment.

All parts, whether in-process or completed, should be transported only in suitable containers incorporating positive means for the isolation of parts from each other. Suitable provisions should be made for the clearance of protruding components including rivets, screws and similar details.

Since the adoption of these relatively simple precautions literally hundreds of skin panels of a particular space vehicle have been fabricated with negligible rejections due to in-process handling and storage damage.

Beryllium is easily painted if the surface is clean. The cleaning methods previously discussed are entirely suitable, if acetone is used for the final solvent-wiping of the surfaces. MEK and toluene leave a slight residue which may inhibit good surface adhesion.

Organic coating such as acrylic primers and lacquers frequently are used as protective coating or as thermal control surfaces. The primer coat should be applied to a dry-film thickness of approximately 0.0005 - 0.0007 and cured for one hour at room temperature prior to the application of the top coat. After the final coat has cured, the parts should again be wrapped in the neutral paper for additional protection.

SECTION IV. CONCLUSIONS

As required during beryllium fabrication operations, the solvent-wiping of the surfaces with lint-free cloth or "Kimwipes," and methyl ethyl ketone (MEK) simply and successfully serves for the removal of lubricants, layout dye, and other superficial contaminants. Deeply etched fingerprints, the heavy oxide film built up during "hot forming," and other gross contaminants may be removed by wet sanding followed by light etching (approximately 0.0005 per surface).

Satisfactory procedures have been developed for the cleaning of beryllium in preparation for subsequent operations such as bonding, plating, and surface coating (painting).

With normal care, and the observance of a few simple handling and storage precautions, beryllium can be processed with the same degree of confidence as conventional aerospace materials.

In conclusion, additional surface treatment development work is recommended. Although satisfactory plating has been accomplished on a laboratory scale, further investigation and refinement of the processes are required. In addition, due to the present developmental nature of this work, the establishment of routine production procedures has not yet been initiated.

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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