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CHARACTERIZATION OF SURFACES PRIOR TO ADHESIVE BONDING.(U)

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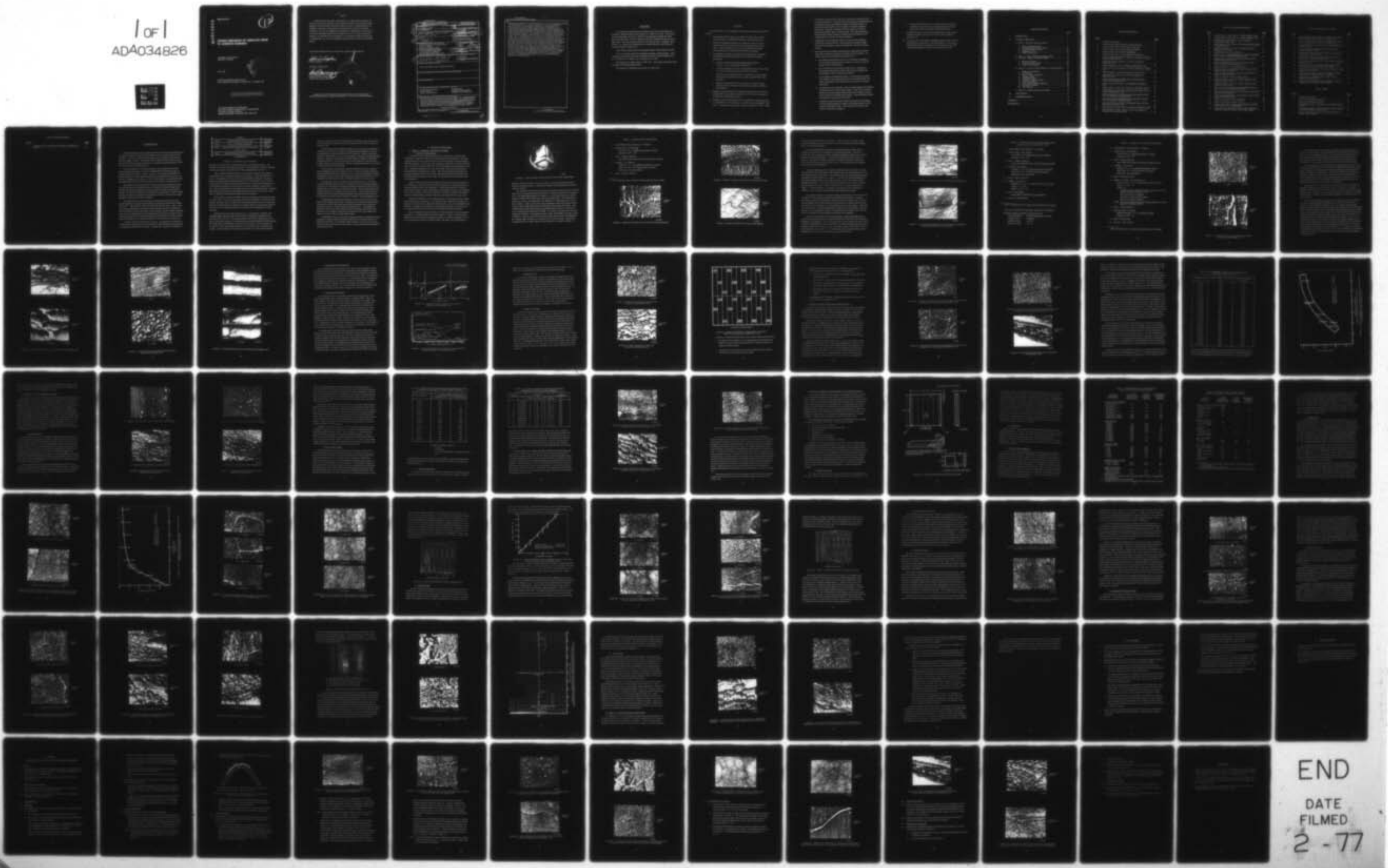

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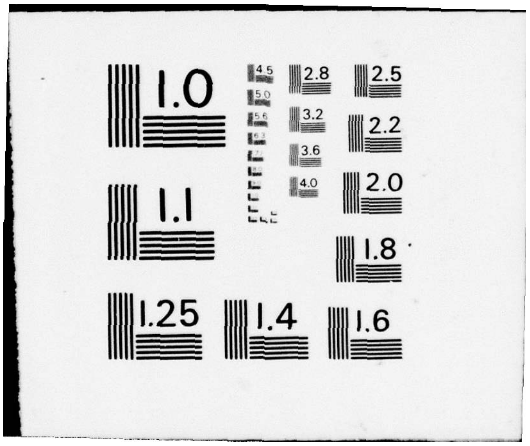
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CHARACTERIZATION OF SURFACES PRIOR TO ADHESIVE BONDING

NORTHROP CORPORATION
AIRCRAFT DIVISION

JULY 1976

TECHNICAL REPORT AFML-TR-76-118
FINAL REPORT FOR PERIOD 15 MARCH 1975 - 15 MARCH 1976

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This technical report has been reviewed and is approved for publication.

John C. Tanzola
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Project Engineer

FOR THE COMMANDER

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Nondestructive Evaluation Branch
Metals and Ceramics Division

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The objective of this program was to develop procedures for the quality control of anodized surfaces on aluminum alloys prior to bonding. The scanning electron microscope (SEM) was selected as the inspection instrument, based on previous experience in which the value of the SEM for analyzing surfaces was demonstrated. Both phosphoric and chromic acid anodizing systems were included in the initial phases of this program. The character of these anodic surface

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coatings was evaluated on both bare and clad 7075-T6 in terms of physical, chemical, and crystallographic nature. Anodic coatings were found to be composed of a porous oxide layer of the boehmite or $\alpha Al_2O_3.H_2O$ crystallographic form. Panels anodized on both the PABST (Primary Adhesively Bonded Structures Technology) program at McDonnell Douglas and Phase II of "Characterization of Surface Prior to Adhesive Bonding" at Rockwell Science Center, exhibited oxide coatings of similar character. The dependence of the anodic film character on the various anodizing parameters was determined for the phosphoric acid anodizing of bare 7075-T6. Included in this investigation were anodizing variables such as voltage, time, bath concentration, pretreatment prior to anodizing, and post-anodize rinsing. Both thickness and cell size of the oxide layer were found to vary almost linearly with the anodizing voltage and parabolically with anodizing time. The oxide character was also found to vary with the concentration of the anodizing bath, with an increase in bath concentration resulting in increases in both oxide thickness and cell size. The anodic surface character determined by SEM inspection prior to adhesive bonding was correlated with the wedge test durability behavior of the bonded surface. Based on this correlation, acceptance and rejection criteria were established for phosphoric acid anodized surfaces. These criteria consisted of a set of SEM photomicrographs taken at various magnifications which characterize the oxide thickness, pore size, cell structure, and uniformity. An anodized surface which matches these photomicrographs is acceptable for adhesive bonding.

FOREWORD

This report was prepared by the Northrop Corporation, Aircraft Division, Hawthorne, California under USAF Contract No. F33615-75-C-5143. The contract was performed under Project No. ILIR 0077 and administered under Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Serving as Program Monitors were Captain John C. Tanzola, USAF, and Dr. R. L. Crane of the Nondestructive Evaluation Branch of the Metals and Ceramics Division, AFML/LLP.

This work was initiated with and partially funded by AFML Director's funds.

Mr. T.P. Remmel served as Principal Investigator on this program. Other Northrop personnel who made major contributions in this research program were R. E. Herfert, B. B. Bowen, P.A. Honeycutt, and A. Hall.

The contractor's report number is NOR 76-58. This report covers work from 15 March 1975 through 15 March 1976.

The report was submitted by the author on 15 April 1976.

SUMMARY

The following are a list of significant results and accomplishments from this program.

1. The Scanning Electron Microscope (SEM) was shown to be a viable inspection tool for evaluating the character of aluminum surfaces.
2. Standard SEM photomicrographs were obtained to show the surface character of 7075-T6 aluminum after various pretreatment process steps. These standards were used for the verification of proper pretreatment prior to anodizing in this and other programs.
3. The evaluation of surface coatings formed by phosphoric and chromic acid anodizing of both clad and bare 7075-T6 led to the following conclusions:
    a. In all cases, the anodic coating consists of the boehmite ($\alpha Al_2O_3 \cdot H_2O$) crystallographic oxide form.

    b. The anodic coatings are nearly contaminant-free but they do contain some trace alloying elements from the base material.

    c. Phosphoric acid anodizing of 7075-T6 results in an anodic coating thickness of about 4000Å on the bare alloy and about 7000Å on the clad alloy.

    d. Chromic acid anodizing of 7075-T6 results in an anodic coating thickness of about 20,000Å on the bare alloy and about 40,000Å on the clad alloy.
4. Phosphoric acid anodizing of 7475 results in the formation of an anodic coating which is very similar to that found on 7075 in terms of physical, chemical and crystallographic nature.
5. Phosphoric acid anodizing of bare 7075-T6 produces an oxide coating that is reproducible in terms of physical, chemical, and crystallographic character. The thickness of this anodic coating was found to be 4100Å ± 400Å.

6. Coordination of the activities in the area of anodic film characterization was conducted between: the PABST (Primary Adhesively Bonded Structures Technology) program at McDonnell Douglas, Long Beach; Phase I of Characterization of Surfaces Prior to Adhesive Bonding at Northrop Corporation, Hawthorne; and Phase II of this program at Rockwell International Science Center, Thousand Oaks. This effort established baseline anodic surface character resulting from the phosphoric acid anodizing that was common to all three programs.

7. A dependence of the anodic film character on the various anodizing parameters was demonstrated. These parameters included voltage, time, bath concentration, specimen pretreatment, and post-anodizing rinsing.

8. The environmental durability testing program established the relationship between anodic film character and adhesive bond durability. The major conclusions reached through this effort were:

   a. The wedge test durability of bare 7075-T6 anodized in phosphoric acid is directly dependent upon the thickness, pore size, and cell structure of the anodic coating.

   b. SEM examination of the anodized surfaces prior to bonding can discriminate between those surfaces that will be acceptable and unacceptable in terms of wedge test durability.

   c. The phosphoric acid anodizing system is very forgiving and rather gross changes in the anodizing procedure are necessary before the wedge test durability of the bonded anodic surface will be changed appreciably.

   d. The phosphoric acid electrolyte, with no voltage applied, has sufficient strength to dissolve a prior anodic coating. Thus, the time interval between the end of anodizing and the beginning of rinsing is critical to the retention of a durable anodic coating. This time interval should be limited to a maximum of two minutes.

   e. Complete omission of the pretreatment process prior to anodizing did not appreciably affect the wedge test durability of bare 7075-T6 anodized in phosphoric acid. This result was not expected, and requires additional investigation.

f. The exposure of phosphoric acid anodized specimens to ambient conditions for three weeks prior to bonding had no detrimental effect on the wedge test durability of the bonded surface.

9. Detailed procedures were prepared for performing the quality control inspection of production panels of bare 7075-T6 alloy anodized in phosphoric acid.

10. The criteria for evaluating the acceptability of anodic surfaces in terms of durability were documented. This documentation is in the form of SEM photomicrographs and thickness data for phosphoric acid anodic coatings exhibiting both acceptable and unacceptable durability.

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I. INTRODUCTION

Adhesive bonding has shown excellent potential for producing aircraft structures of improved structural integrity and durability as well as reduced weight and cost. Therefore, a great deal of effort has been applied to the development of structural adhesive bonding. However, the benefits of this technique cannot be fully realized until proper quality assurance techniques are developed and implemented for each of the critical steps of the bonding process.

A major problem area in adhesive bonding is the reliability of the surface preparation prior to bonding. It has been established that anodizing provides an excellent surface for adhesive bonding. However, the integrity and durability of a bonded structure are heavily dependent upon the oxide characteristics such as composition, morphology, and thickness. Prior to this program, no procedure had been developed which would assure that the proper oxide character had been achieved.

The objective of this program was to develop operating procedures for using the scanning electron microscope (SEM) as a technique for characterizing anodic coatings and to develop standards for quality control of anodized surfaces prior to bonding. The selection of the SEM was based upon past experience, which has shown that this instrument is invaluable for the analysis of surface coatings and is readily adaptable to monitoring of surface reliability.

The model shown in Figure 1 has been developed to explain the role of the aluminum/adhesive interface in determining the strength and durability of a bonded structure(1). The interfacial region may be divided into four zones. Zones 1 and 4 are presently undefined and contain the complex chemical reaction constituents of either the adhesive and the oxide layer or the oxide layer and the aluminum substrate. These zones are important from the standpoint that the chemical reactions in Zone 1 may adversely affect the environmental resistance of the adhesive, and the mechanochemical reactions in Zone 4 affect the adhesion of the oxide to the metal surface.

In Zone 2, the desired oxide form is $\alpha Al_2O_3 \cdot H_2O$ (boehmite), which can be induced on the surface by specific chemical and/or electrochemical processing such as anodizing or metalbond FPL etching. The thickness, character, and tenacity of

	ADHESIVE	
ZONE 1.	ADHESIVE-OXIDE INTERACTION ZONE	1000-5000 Å
ZONE 2.	$\alpha Al_2O_3 \cdot H_2O$ (POROUS OR BARRIER)	0-5000 Å
ZONE 3.	RESIDUAL OXIDE OR PRE-ANODIZE CREATED OXIDE $\beta \cdot Al_2O_3 \cdot 3H_2O$	50-1000 Å
ZONE 4.	MECHANO-CHEMICAL REACTION WITH METAL	UNDEFINED
	ALUMINUM ALLOY	

FIGURE 1. INTERFACIAL ZONE MODEL

the oxide in this layer can be controlled by proper processing procedures. The boehmite oxide layer, when adhesively bonded, forms the highest initial bond strength and is the most environmentally stable surface coating known at this time.

Zone 3, the third interfacial layer, is the weakest link between the adhesive and the metal and is characterized mainly as the $\beta Al_2O_3 \cdot 3H_2O$ (bayerite) form of oxide. The weakness in this layer lies in the tendency of the bayerite, which lies between the metal surface and the boehmite layer, to grow in the presence of moisture and stress, resulting in failure through the oxide. Bayerite forms naturally in a reaction between aluminum and moisture from ambient conditions to about 150F to 160F, and is normally found on the surfaces of as-received aluminum sheets. Optimum bond durability is achieved by reducing the thickness of the bayerite layer to a minimum by chemically deoxidizing the surface prior to anodizing.

This program is concerned with the control and inspection of the oxide character in Zones 2 and 3. These have the greatest effect on the durability of an adhesive bond. Based on the above model, the path to the most durable adhesive bond is to reduce the thickness of the bayerite layer (Zone 3) to less than 100Å and to increase the boehmite layer (Zone 2) to an optimum thickness for maximum bond strength and corrosion resistance.

Included in the scope of this program were: (1) the physical, chemical, and crystallographic characterization of anodic films resulting from phosphoric acid anodizing of bare 7075-T6, (2) the determination of the effect of sample size on the nature of the anodic coating, (3) the demonstration of the applicability of SEM inspection for verifying the reproducibility of the anodic film character, (4) the evaluation of the effect of various anodizing parameters on the character of the resulting anodic coating, (5) the correlation of environmental durability of a bonded surface with the character of the anodized surface determined prior to bonding, and (6) the determination of acceptance and rejection criteria for the surface of bare 7075-T6 anodized in phosphoric acid.

In the first phase of this program procedures were developed for morphological characterization of anodic oxide layers resulting from both phosphoric and chromic acid anodizing of clad and bare (unclad) 7075-T6 aluminum. Included was the determination of oxide thickness, pore size, cell structure, chemistry, and crystallographic character. Physical characterization was performed by examination of the anodic coating using the SEM. The chemical character of the anodic films was determined by Auger electron spectroscopy (AES), while the crystallographic nature of the coating was determined by electron diffraction.

The second phase of the program involved a definitive study on the reproducibility of phosphoric acid anodizing of bare 7075-T6. Numerous repetitive anodizing runs at standard condition were conducted over a period of approximately nine months. The character of the resulting anodic coatings was evaluated to determine the reproducibility of the anodizing system and to establish standards for the oxide layer.

The third phase involved coordination of the efforts between: (1) the PABST (Primary Adhesively Bonded Structures Technology) Program at McDonnell Douglas, Long Beach, (2) Phase II of this program being conducted at Rockwell Science Center, Thousand Oaks, and (3) Phase I, conducted at Northrop. This coordination phase was conducted to insure a free exchange of ideas, specimens, and data between the three programs and to insure that the baseline phosphoric acid anodic surfaces formed in each program were equal in terms of physical, chemical, and crystallographic nature.

The fourth phase correlated the anodic film character with the environmental behavior of the bonded anodic surface. Wedge tests were conducted on bonded panels made with bare 7075-T6 sheets that were anodized in phosphoric acid with various conditions to produce a variety of anodic film characteristics. The durability of these panels was then correlated with the anodic film character determined by SEM inspection prior to bonding to establish the characteristics of anodic surfaces that either do or do not result in a durable adhesive bond.

The fifth phase of this program dealt with the preparation of a standard operating procedure for using the SEM/Mini-SEM for quality control of anodized surfaces in a production environment. This included surface reliability, acceptance and rejection criteria, as well as documentation of the problem areas associated with the phosphoric acid anodizing process.

II. TECHANICAL DISCUSSION

A. PHASE I – BASELINE ANODIZATION STUDIES

1. Physical Characterization

The physical characteristics of the surface coatings in this program were evaluated by examination with the SEM (Scanning Electron Microscope). All of the anodized specimens were prepared for SEM examination using a 90° bend technique. With this technique, the specimen, approximately 0.125-inch by 1-inch by 0.063-inch thick, was bent to an angle of about 90°, or until the aluminum surface began to fracture. During this bending process, the more brittle oxide coating cracked but remained attached to the aluminum surface. After being coated with a thin layer of gold (approximately 200Å) to insure proper specimen grounding and to enhance the secondary electron emission of the surface, the specimen was inserted in the SEM for examination.

Figure 2 shows a SEM specimen holder with four bend specimens mounted on it. The holder is inserted in the SEM and the specimens are examined along the two viewing directions shown in the photograph. Examination along the A-Direction, normal to the surface, reveals information on the porosity, structure, and uniformity of the surface coating. Examination along the B-Direction, parallel to the surface, shows the coating thickness as well as the cross-sectional structure of the oxide.

Of primary importance in any anodizing process is the proper treatment of the base material prior to anodizing. Past experience has indicated that improper pretreatment can result in poor anodic film characteristics, such as uncontrollable oxide thickness, improper cell development, wrong oxide composition, weak adhesion of the anodic film to the base metal, and poor durability of the bonded surface.

The pretreatment processing of the as-received material used in this program consisted of: (1) trichloroethane vapor degreasing for removal of soluble organic materials deposited during processing and handling, (2) alkaline cleaning in a Turco 4215-S solution for removal of insoluble organic materials, and (3) deoxidizing in

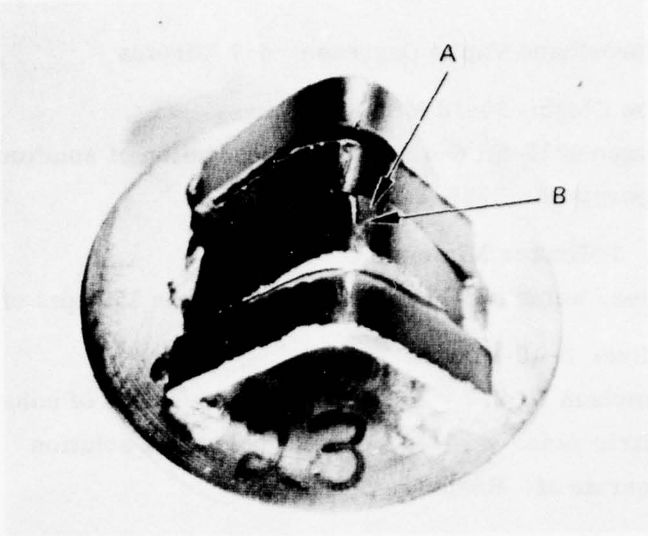


FIGURE 2. SEM SPECIMEN CONFIGURATION AND VIEWING DIRECTIONS

Amchem 7 and nitric acid for removal of residual surface oxide generated during mill processing and storage. A complete description of the pretreatment procedures is given in Table 1.

The character of the surfaces of both bare and clad 7075-T6 sheets was evaluated after each of the pretreatment processing steps to establish a baseline for subsequent work. The SEM photomicrographs in Figures 3, 4, and 5 depict the typical surface character of bare 7075-T6 after each of the pretreatment steps. These photomicrographs were taken at a magnification of 14,000X with a viewing perspective normal to the surface. Figure 3, taken after vapor degreasing, shows clear evidence of the residual surface oxide which had formed during mill processing and handling. This residual bayerite oxide exists on all as-received aluminum sheets. It was found to vary in thickness from about 500Å to 2000Å. The cracks in the oxide were caused by bending the specimen. The appearance of the surface after alkaline cleaning is shown in Figure 4. This step removed the insoluble organic material that was imbedded in the residual oxide, resulting in a somewhat porous surface coating. Following the deoxidizing step, the surface appears nearly oxide-free, as shown in Figure 5. A

TABLE 1. PRETREATMENT PROCEDURE

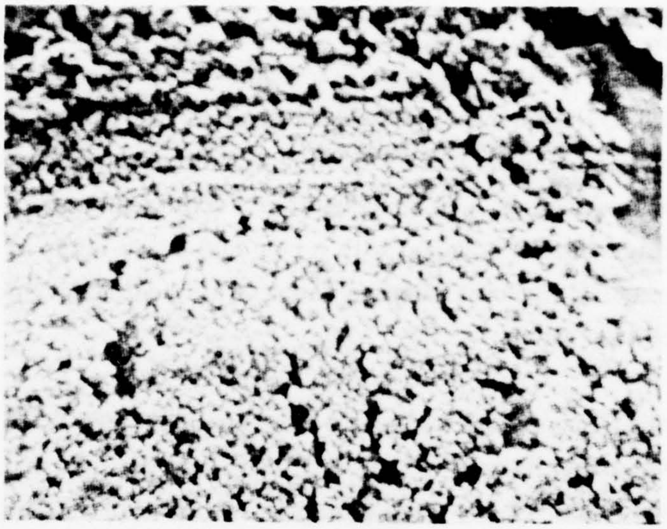
1. Trichloroethane Vapor Degrease: 4-7 Minutes
2. Alkaline Clean: 10-15 Minutes
   - Turco 4215-S: 6-8 weight ounces/gallon of solution
   - Operate at: 155F ± 10F
3. Rinse: 5 Minutes Minimum
   - Rinse water shall contain not more than 150 ppm of solids
4. Deoxidize: 5-10 Minutes
   - Amchem 7: 2.7 - 3.3 weight ounces/gallon of solution
   - Nitric Acid: 8% - 16% of total volume of solution
   - Operate at: Room temperature
5. Rinse: 5 Minutes Minimum

NOTE: Deionized water was used in mixing solutions and in rinsing.

NORMAL
VIEW

14,000X

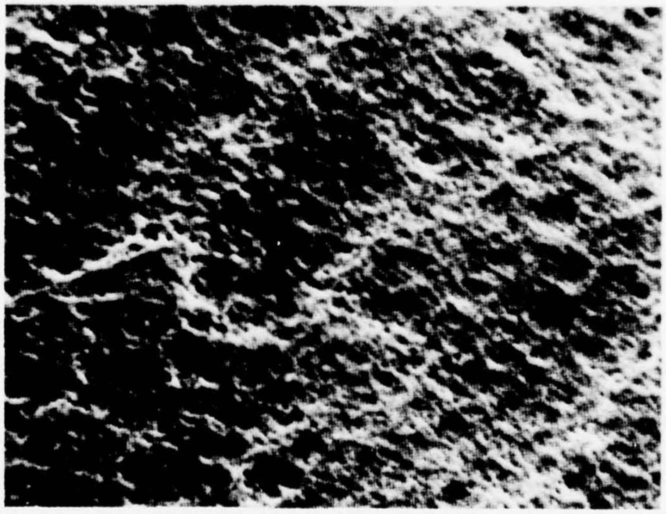
FIGURE 3. SURFACE OF BARE 7075-T6 AFTER VAPOR DEGREASING



NORMAL
VIEW

14, 000X

FIGURE 4. SURFACE OF BARE 7075-T6 AFTER ALKALINE CLEANING



NORMAL
VIEW

14, 000X

FIGURE 5. SURFACE OF BARE 7075-T6 AFTER DEOXIDIZING

thin layer of oxide still exists on the surface (<100Å). However, this layer cannot be detected with the SEM and is believed to be removed in both the chromic and phosphoric acid anodizing solutions.

It is generally felt that the existence of a nearly oxide-free surface prior to anodizing is essential to the formation of a durable anodic surface. Therefore, a periodic check of the surface character following deoxidizing was performed to insure proper pretreatment processing. An unacceptable deoxidized surface is shown in Figure 6. This surface is still covered with a residual oxide layer in which oxide pores as well as some cell structure can be seen. This residual oxide is estimated to be on the order of 400Å thick.

The etched appearance of the correctly deoxidized surface in Figure 5 is due to the acidic nature of the deoxidizer, which dissolves away the residual oxide as well as some of the underlying base metal. The etch pits seen in this photomicrograph appear considerably smaller than those in Figure 7. The latter SEM photomicrograph is of the same deoxidized surface as that shown in Figure 5, but it was taken at a lower magnification (2800X). The larger etch pits are indicated by the arrows. Note also the deep etching of the grain boundaries along the left- and right-hand borders of Figure 7. These boundaries are important, since they are a clear indication of whether or not a surface has gone through the deoxidizing step properly.

The baseline character of the oxide coatings on bare and clad 7075-T6 from both phosphoric and chromic acid anodizing was established in this phase. Complete descriptions of these two anodizing procedures are given in Tables 2 and 3. Physical characterization of the anodized surfaces was performed by inspection with the SEM. Characteristics of the oxides, such as thickness, pore size, cell structure, uniformity of coating coverage, and second-phase particle effects, were documented. Figures 8 through 11 are SEM photomicrographs of the typical anodic coatings on bare and clad 7075-T6 resulting from both phosphoric and chromic acid anodizing.

Figure 8, taken normal to the specimen surface, compares the differences in oxide cell character between the anodized surfaces of bare and clad 7075-T6 following phosphoric acid anodizing. The cell structure of the anodic coating on the bare 7075-T6 is much coarser than that formed on clad 7075-T6, and the oxide pore size on the bare surface is larger than on the clad. Thus, the anodic coating on clad 7075-T6 is more dense than that on bare 7075-T6. The cracks in the anodic coatings shown in these photographs are caused by the bending of the aluminum specimen.

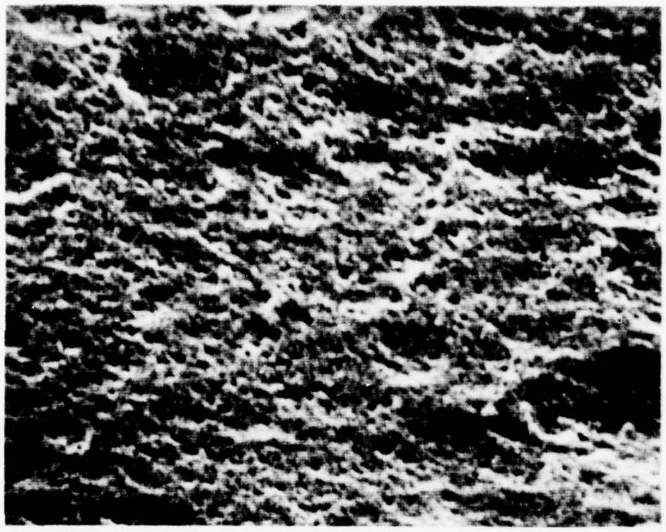


FIGURE 6. SURFACE OF BARE 7075-T6 AFTER IMPROPER DEOXIDIZING

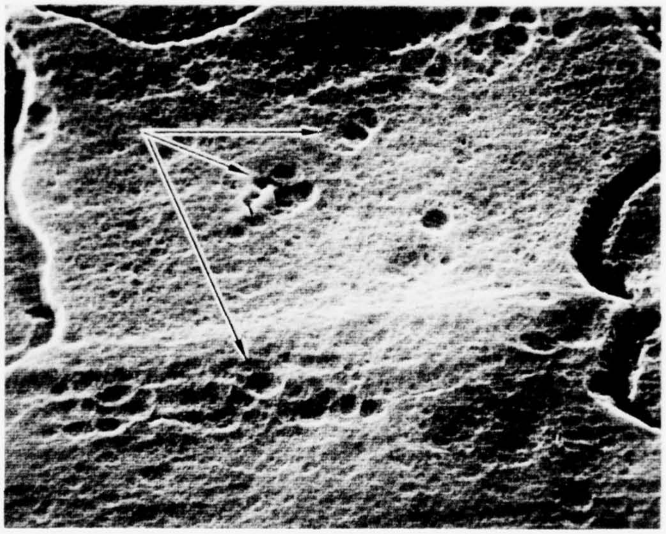


FIGURE 7. ETCH PITS AND GRAIN BOUNDARY ETCHING OF A PROPERLY DEOXIDIZED SURFACE OF BARE 7075-T6

TABLE 2. PHOSPHORIC ACID ANODIZING PROCEDURE
(Boeing Process Specification BAC-5555)

1. Trichloroethane Vapor Degrease: 4-7 Minutes

2. Alkaline Clean: 10-15 Minutes

   Turco 4215-S: 6-8 weight ounces/gallon of solution

   Operate at: 155F ± 10F

3. Rinse: 5 Minutes Minimum

   Rinse water shall contain not more than 150 ppm of solids

4. Deoxidize: 5-10 Minutes

   Amchem 7: 2.7 - 3.3 weight ounces/gallon of solution

   Nitric Acid: 8% - 16% of total volume of solution

   Operate at: Room temperature

*5. Rinse: 5 Minutes Minimum

**6. Anodize: 20-25 Minutes

Phosphoric Acid: 11 - 16 fluid ounces/gallon of solution

Voltage: 10 ± 1 volt

Operate at: 65F - 85F

7. Rinse: 10-15 Minutes

   Rinse within 2 minutes after current stopped

8. Oven Dry: 160F Maximum

NOTE: Deionized water was used in mixing solutions and in rinsing.

* Parts must be processed in continuous sequence from 5 through 8.

** Standard anodizing conditions for this program are:

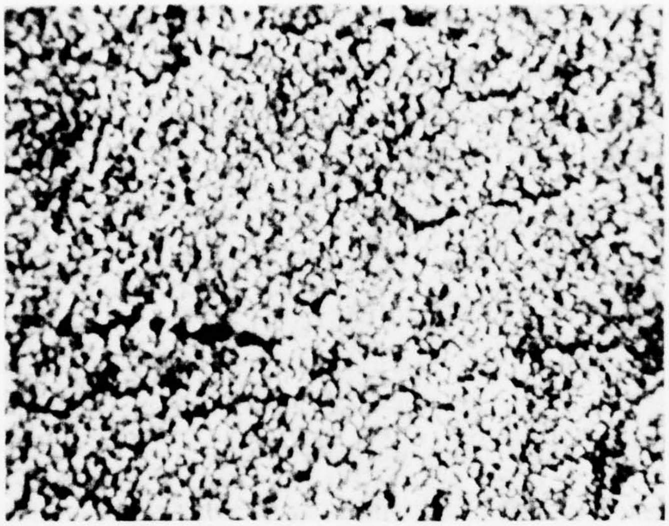
Bath Concentration:	14 fluid ounces/gallon of solution
Anodizing Time:	20 minutes
Anodizing Voltage:	10 volts
Bath Temperature:	75F ± 5F

TABLE 3. CHROMIC ACID ANODIZING PROCEDURE

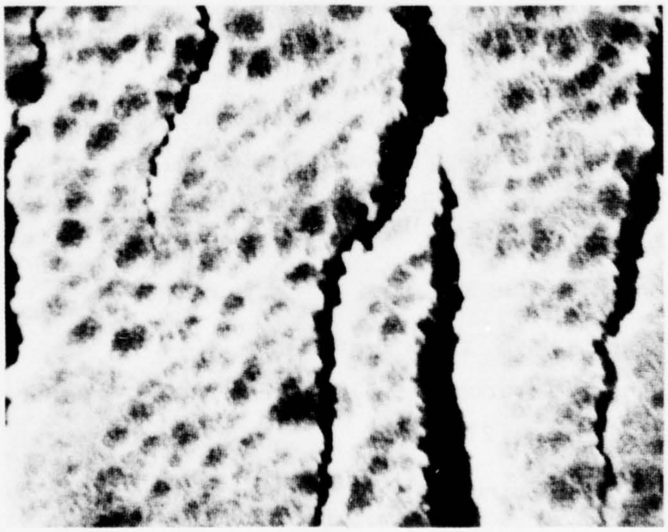
1. Trichloroethane Vapor Degrease: 4-7 Minutes
2. Alkaline Clean: 10-15 Minutes
    - Turco 4215-S: 6-8 weight ounces/gallon of solution
    - Operate at: 155F ± 10F
3. Rinse: 5 Minutes Minimum
    - Rinse water shall contain not more than 150 ppm of solids
4. Deoxidize: 5-10 Minutes
    - Amchem 7: 2.7 - 3.3 weight ounces/gallon of solution
    - Nitric Acid: 8% - 16% of total volume of solution
    - Operate at: Room temperature
5. Rinse: 5 Minutes Minimum
6. Anodize: 40 Minutes (See schedule below)
    - Chromic Acid: 6.7 - 13.4 weight ounces/gallon of solution
    - Operate at: 104F ± 4F
    - Voltage: DC
        - Gradually increase voltage for first 10 minutes from 0 to 40 volts in steps of not more than 5 volts
        - Hold at 40 volts for 20 minutes
        - Increase to 50 volts within 5 minutes
        - Hold at 50 volts for 5 minutes

    (NOTE: The current density at the higher voltage should be 2.5 amps/square foot of anode surface.)
7. Rinse: 5 Minutes Minimum
8. Dichromate Seal: 15 Minutes
    - Sodium Dichromate: 5.0 - 6.5 percent by weight
    - Operate at: 210F ± 2F
9. Rinse: 10-15 Minutes
10. Oven Dry: 160F Maximum

NOTE: Deionized water was used in mixing solutions and in rinsing.



a. BARE 14,000X



b. CLAD 14,000X

FIGURE 8. OXIDE PORE AND CELL CHARACTER ON 7075-T6 ANODIZED IN PHOSPHORIC ACID

The SEM photomicrographs in Figure 9 show the anodic coatings as viewed through their cross-section. These photographs reveal information on the film thickness as well as its longitudinal structure. The dispersed nature of the oxide is due to the differences in ductility between the brittle anodic film and the ductile base metal, and their relative displacements during the bending and cracking of the 90° bend specimen. In the foreground of Figure 9a is the crack in the base aluminum.

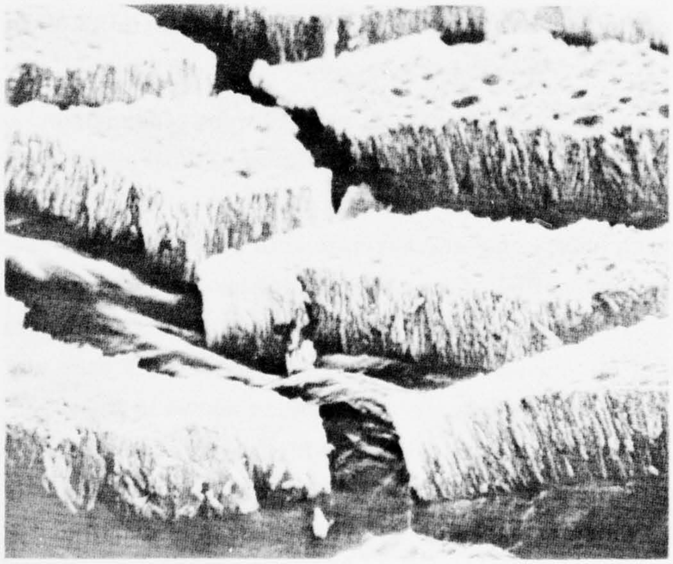
The oxide thickness resulting from phosphoric acid anodizing of bare 7075-T6 is on the order of 4000Å, whereas on clad 7075-T6, the thickness is about 7000Å. These values were determined directly from the photomicrographs by measuring the oxide height and dividing by the magnification. Also shown in Figure 9 is the difference in columnar cell structure between the two anodic coatings. The oxide on the clad 7075-T6 appears to grow in fine vertical columns; whereas, on the bare 7075-T6, the oxide is much coarser and shows evidence of branching during growth (that is, the existence of noncontinuous cells through the oxide thickness).

Anodizing of 7075-T6 in chromic acid also produces a difference in anodic film character between bare and clad surfaces, as shown in Figure 10. As with the phosphoric acid anodizing system, the cell structure of the oxide on the bare material is much coarser than that on the clad; whereas the clad anodic coating is a more dense oxide structure. In addition, the oxide on the clad material is about twice as thick as that on the bare.

The SEM photographs shown in Figure 10 were taken normal to the surface and are similar in both orientation and magnification to those of the surface shown in Figure 8 which was anodized in phosphoric acid. It is difficult to distinguish the difference between phosphoric and chromic acid anodic coatings from these photographs alone. However, inspection of the coating thicknesses reveals the differences between the two anodic coatings, as shown in Figure 11. These SEM photomicrographs of the cross-sections of the chromic acid anodic coatings on both bare and clad 7075-T6 are comparable to those for phosphoric acid anodize shown in Figure 9. However, the magnification in Figure 11 is much less, with the oxide thickness resulting from the chromic acid anodizing of bare 7075-T6 being about 20, 000Å and, of the clad material, about 40, 000Å. This compares to oxide thicknesses of 4000Å and 7000Å resulting from phosphoric acid anodizing of bare and clad 7075-T6. In addition, a comparison of the oxide coating structures in Figures 9 and 11 reveals that the chromic acid anodic coatings do not exhibit the detailed columnar cell structure seen with the phosphoric acid anodic coatings.

PARALLEL
VIEW

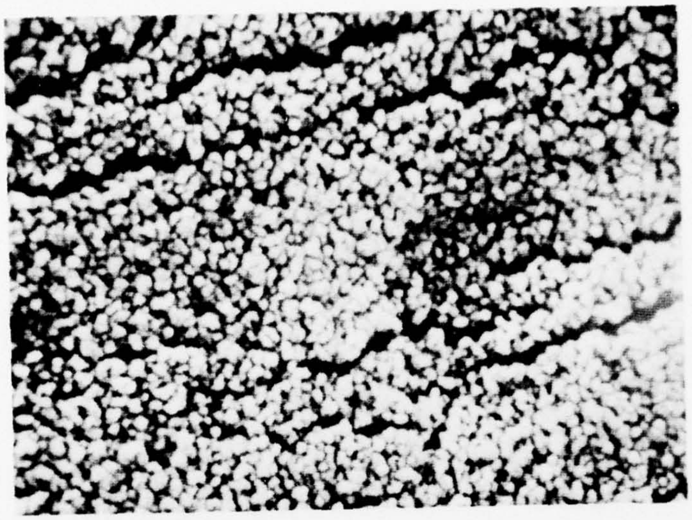
a. BARE 18, 000X



PARALLEL
VIEW

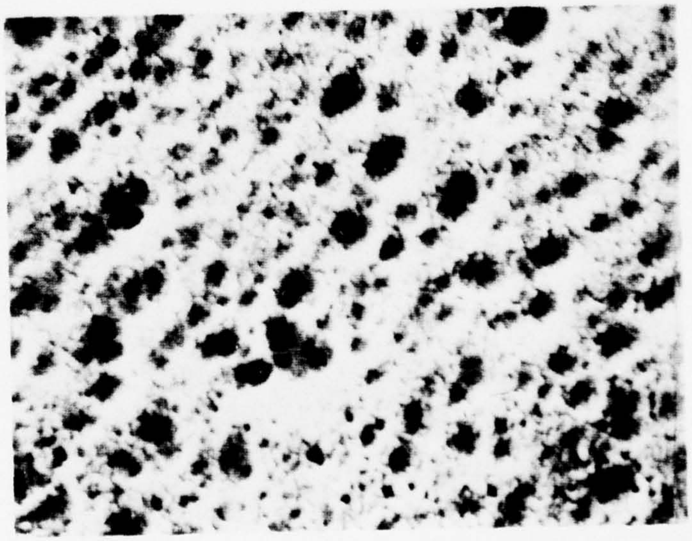
b. CLAD 17, 000X

FIGURE 9. OXIDE THICKNESS ON 7075-T6 ANODIZED IN PHOSPHORIC ACID



NORMAL
VIEW

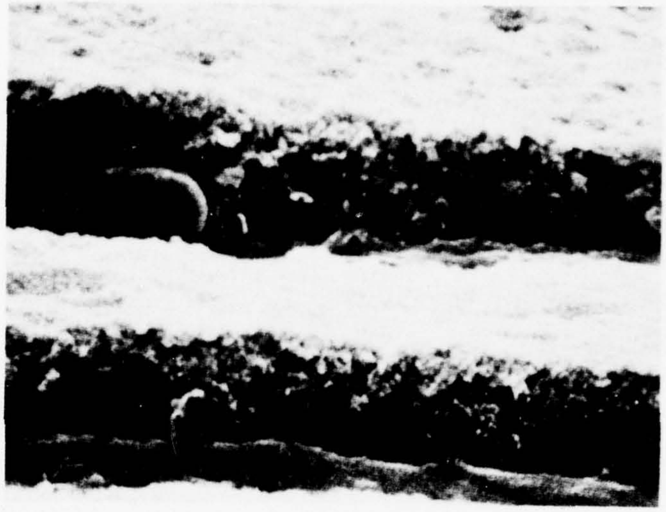
a. BARE 14, 000X



NORMAL
VIEW

b. CLAD 14, 000X

FIGURE 10. OXIDE PORE AND CELL CHARACTER ON 7075-T6
ANODIZED IN CHROMIC ACID



PARALLEL VIEW

a. BARE 9,000X

PARALLEL VIEW

b. CLAD 4,500X

FIGURE 11. OXIDE THICKNESS ON 7075-T6 ANODIZED IN CHROMIC ACID

2. Crystallographic Chracterization

The crystallographic characterization of the anodic coatings resulting from both phosphoric and chromic acid anodizing was performed by electron diffraction using the transmission electron microscope (TEM). Electron diffraction patterns were obtained by reflecting the electron beam from the anodic coating at a low angle. The oxides were left intact on the base alloy for this analysis. This is important, since it is suspected that stripping the oxides from the aluminum changes the crystalline form. Analysis of these patterns showed that all of these anodic coatings were of the boehmite or a $\alpha Al_2O_3 \cdot H_2O$ crystalline structure. This is the desirable oxide form for adhesive bonding because of its stability and durability in the presence of stress and moisture.

3. Chemical Characterization

The chemical character of the baseline anodic films was determined by Auger electron spectroscopy (AES), coupled with sputter-ion depth profiling. Figure 12 shows a typical Auger spectrum from the surface of a phosphoric acid anodic coating on bare 7075-T6. This spectrum reveals chemical information from only the outer 8 to 20Å of the anodic film. It is a derivative plot of the number of electrons as a function of electron energy. The peaks on this spectrum correspond to the various elements present on the surface, with the peak-to-peak amplitude being generally indicative of the amount of that element present. This spectrum shows a nearly contaminant-free surface following the phosphoric acid anodizing of 7075-T6, with phosphorus, sulfur, chlorine, carbon, nitrogen, iron, copper, zinc, and magnesium being present in trace amounts in the outer layers of the anodic coating. The copper, zinc, and magnesium are from the alloy constituents in the aluminum. The phosphorous in the coating is from the anodizing bath. The other trace elements are from either the rinse water or exposure to atmospheric conditions.

By simultaneously performing Auger electron spectroscopy and ion sputter etching, one can obtain information on the distribution of the trace elements throughout the anodic coating. Shown in Figure 13 is a plot of the distribution of some of the elements through the oxide thickness obtained by Auger spectroscopy/ion sputtering. This plot shows that both zinc and magnesium are concentrated mainly in the outer 20Å of the anodic coating. It is significant to note that the amounts of both of these elements are higher in the outer surface layers of the anodic coating than they are in the base alloy itself. Also seen in Figure 13 is the presence of phosphorus throughout the anodic coating, with a higher concentration in the outer 50Å to 100Å of the coating.

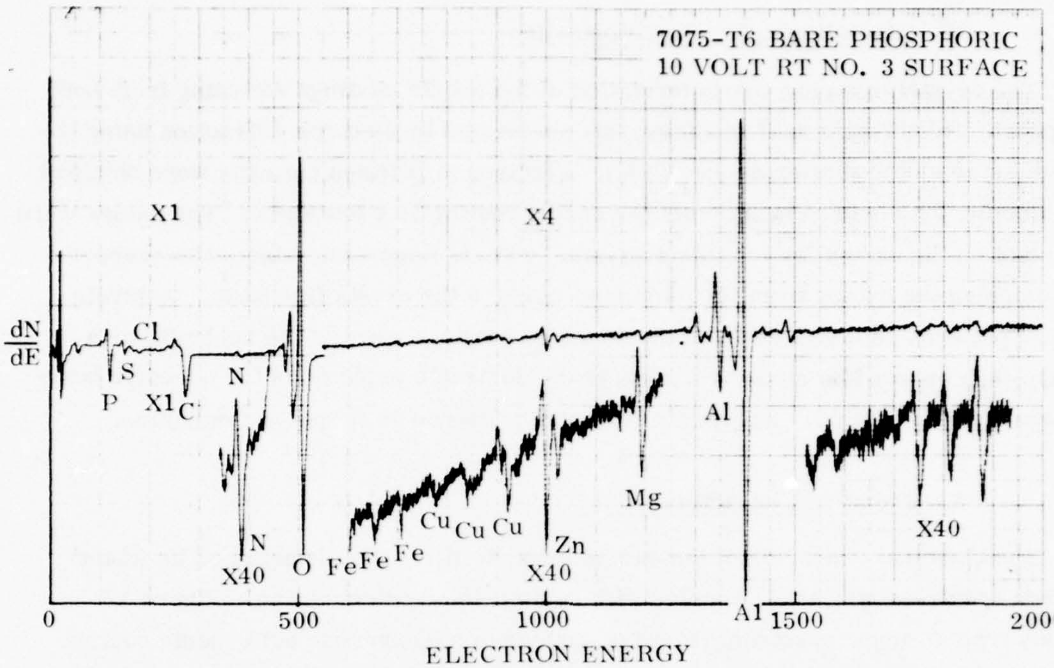


FIGURE 12. AUGER SPECTRUM OF BARE 7075-T6 SURFACE ANODIZED IN PHOSPHORIC ACID

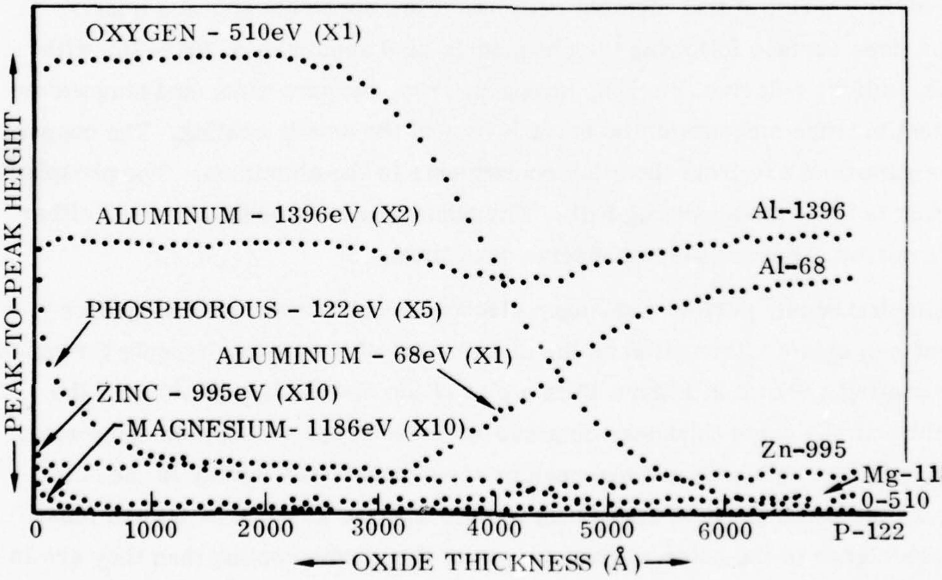


FIGURE 13. AUGER ELEMENTAL DEPTH PROFILE OF BARE 7075-T6 SURFACE ANODIZED IN PHOSPHORIC ACID

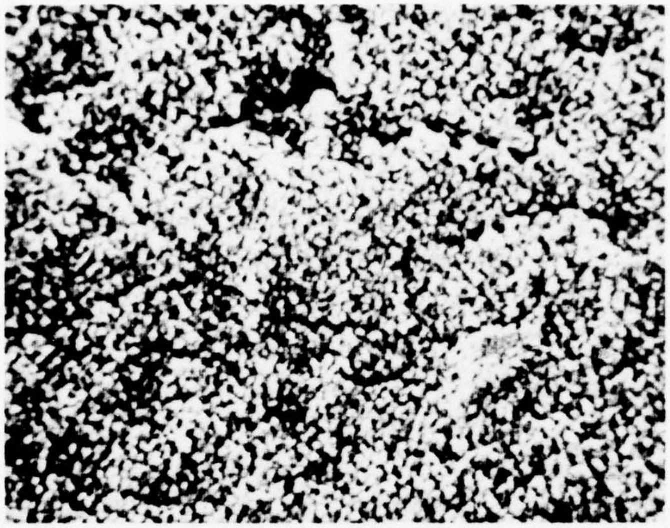
Although not shown here, trace elements such as nitrogen, carbon, sulfur, iron, and copper normally exist only in the outer 20Å to 50Å of the anodic coating.

4. Anodizing of 7475

In this phase of the program, a study was conducted to determine whether the inspection procedures developed for 7075 are also applicable to 7475 aluminum alloy. Shown in Figures 14 and 15 are SEM photomicrographs of the phosphoric acid anodic coating on bare 7475. These photomicrographs are of the same orientation as those of the phosphoric acid anodic coatings on bare 7075, shown in Figures 8a and 9a. No differences could be detected between the cell structure, pore size, and general uniformity of the oxides on 7075 and 7475. The chemical and crystallographic character of the anodic coatings on the two alloys were identical, both being of the boehmite form and nearly contaminant free. Only a slight difference in oxide thickness could be found between the two alloys, with the 7075 anodic coating being about 200Å thicker than that of 7475. However, it was felt that this difference is insignificant and that the SEM inspection techniques are applicable to both alloys.

5. Effect of Sample Size

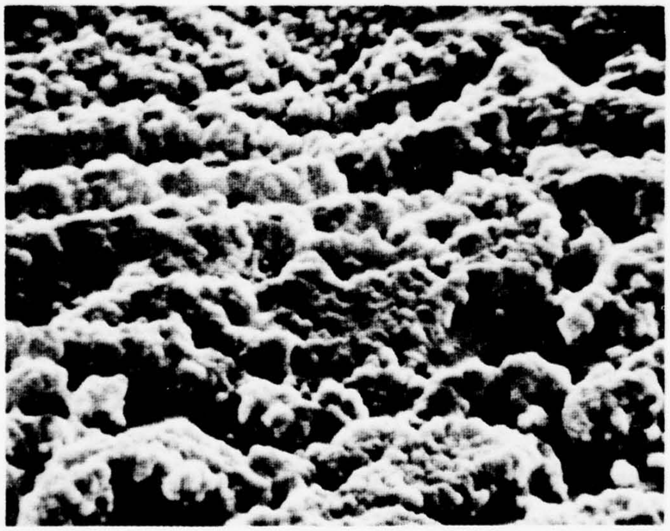
The effect of sample size on the character of the anodic coating was also investigated in this phase. A 12-inch by 12-inch panel and a 1-inch by 1-inch specimen of bare 7075-T6, both 0.063-inch thick, were anodized simultaneously in a phosphoric acid bath at standard conditions. The larger panel was sectioned and systematically inspected using the SEM for documentation of the character of the oxide coating as a function of position on the panel. Shown in Figure 16 is a schematic drawing of the 12-inch square panel, along with the oxide thickness from the various areas of the panel. The oxide was found to be consistent across the panel in terms of physical morphology, such as pore size, cell structure, and coating uniformity, as well as thickness, which was 4100Å ± 400Å. This variation is within the accuracy of the thickness measuring technique. Comparison of the anodic coating on the 12-inch by 12-inch panel with that on the 1-inch by 1-inch coupon revealed no differences in either physical, chemical, or crystallographic character. The oxide thickness on the smaller coupon was measured to be 4000Å ± 400Å. Therefore, it was concluded that, for the relative sample sizes studied, there was no dependence of the anodic coating character on the panel size.



NORMAL
VIEW

14,000X

FIGURE 14. OXIDE CELL STRUCTURE ON BARE 7475 ANODIZED IN PHOSPHORIC ACID



PARALLEL
VIEW

18,000X

FIGURE 15. OXIDE THICKNESS ON BARE 7475 ANODIZED IN PHOSPHORIC ACID

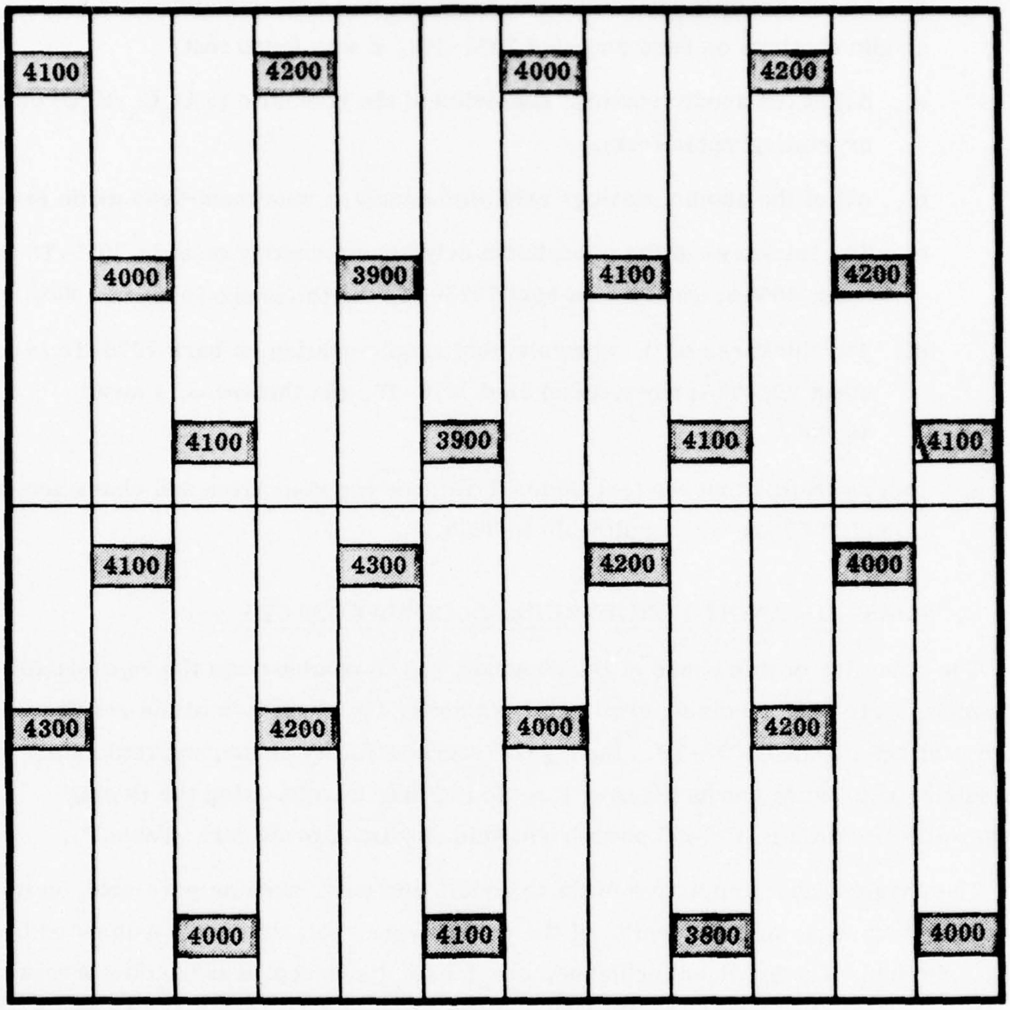


FIGURE 16. OXIDE THICKNESS (IN Å) VERSUS PANEL LOCATION — BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

In summary, the effort during this phase of the program resulted in the following:

1. Development of the techniques for, and demonstration of the feasibility for, using the scanning electron microscope (SEM) to evaluate the character of anodized aluminum surfaces.

2. Establishment of the character of bare and clad surfaces of 7075-T6 after each of the three pretreatment processing steps.

3. Determination of the baseline character of phosphoric and chromic acid anodic coatings on bare and clad 7075-T6. It was found that:
   a. All of the anodic coatings consisted of the boehmite (α $Al_2O_3 \cdot H_2O$) oxide crystallographic form.
   b. All of the anodic coatings exhibited nearly contaminant-free oxide layers.
   c. The thickness of the phosphoric acid anodic coating on bare 7075-T6 is about 4000Å; whereas on clad 7075-T6, the thickness is about 7000Å.
   d. The thickness of the chromic acid anodic coating on bare 7075-T6 is about 20,000Å; whereas on clad 7075-T6, the thickness is about 40,000Å.
4. Determination that the techniques developed for inspection and characterization of 7075 are also applicable to 7475.

B. PHASE II – ANODIC OXIDE REPRODUCIBILITY STUDY

The objective of this phase of the program was to demonstrate the reproducibility of the phosphoric acid anodizing system by evaluating the character of the resulting anodic coatings on bare 7075-T6. During the reproducibility phase, approximately 30 anodizing runs were conducted over a period of nine months using the Boeing Process Specification BAC-5555 phosphoric acid anodizing procedure (Table II).

The physical characteristics of these anodic coatings, such as pore size, cell structure, thickness, and uniformity of the oxide, were evaluated and documented by SEM inspection. The 90° bend technique, previously discussed, was used to prepare the specimens for the SEM. The SEM photomicrographs of the surfaces, shown in Figures 17, 18, 19, and 20, are typical of the reproducibility specimens after phosphoric acid anodizing. These four photomicrographs represent the recommended standard inspection procedure and magnifications for documenting the anodic surface character which was developed and used in this program.

Three of the photomicrographs, Figures 17, 18, 19, are taken along a viewing direction normal to the surface plane at increasing magnifications. Figure 17, taken at a magnification of 700X, shows the general uniformity of the anodized surface, as well as defects in the coating such as holes due to localized attack of dispersoids or second phase particles at the surface. The etching of the grain boundaries, due to the deoxidizing step immediately preceding anodizing, is also visible in this photomicrograph, but is more readily apparent in Figure 18, taken at a magnification of

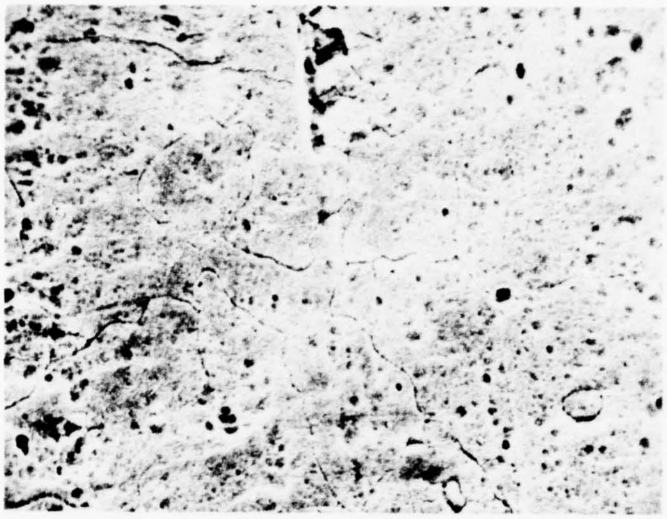


FIGURE 17. GENERAL UNIFORMITY OF ANODIC COATING ON THE SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

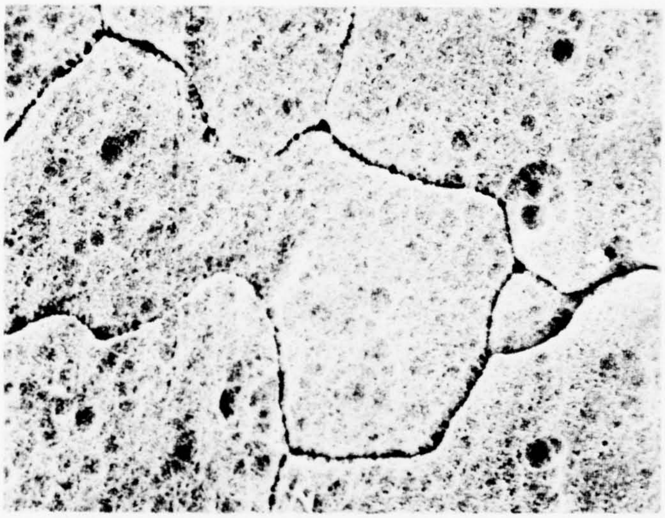


FIGURE 18. PREVIOUSLY ETCHED GRAIN BOUNDARIES ON THE SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

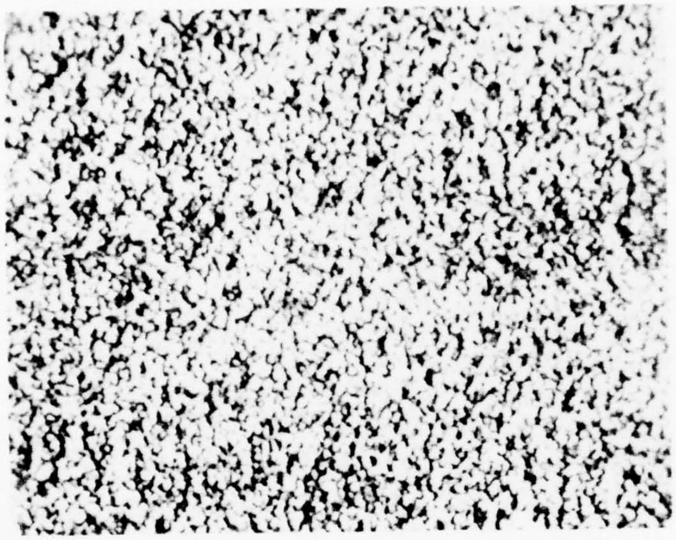


FIGURE 19. PORE SIZE AND CELL STRUCTURE ON THE SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

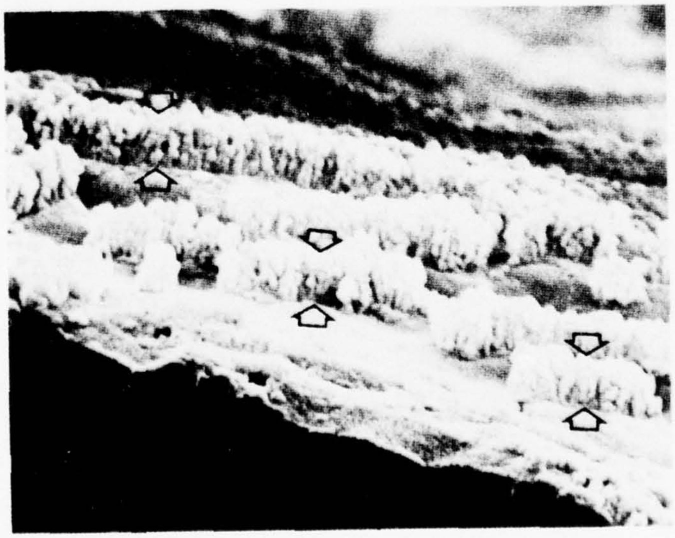


FIGURE 20. OXIDE THICKNESS ON BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

2800X. A qualitative assessment of the grain boundary attack can be made from this photograph. Also note the presence of large and small etch pits in the surface. This structure confirms that the deoxidation procedures were performed correctly.

A comparison between the anodized surface shown in Figure 18 and the deoxidized surface shown in Figure 7 reveals only a slight difference in appearance between the two. This difference is the presence of a porous oxide coating on the anodized surface which is barely visible at a magnification of 2800X, but is easily seen when inspected at higher magnifications, as shown in Figure 19. This SEM photomicrograph, taken at a magnification of 14,000X, verifies the presence of the porous anodic coating on the surface and also yields information on the pore size and cell structure of the oxide.

The thickness of the anodic coating is determined by viewing the cracked oxide through its cross-section, as shown by the SEM photomicrograph in Figure 20. The oxide thickness is derived directly from the photomicrograph by measuring from the bottom of the oxide, at the oxide-metal interface, to the top or outer extremes of the anodic coating. In most cases, the angle relative to the oxide cross-section at which these photomicrographs are taken is not precisely known. Therefore, the measured thicknesses may be less than the true oxide thickness. However, differences in thickness resulting from this uncertainty are estimated to be less than 5% for a typical analysis and were ignored on this program due to the 10% accuracy limitation of the thickness measuring technique. The accuracy limitation was established in the reproducibility study, Phase II of this program.

Oxide thicknesses for all of the reproducibility study specimens were determined by SEM inspection by the aforementioned technique. Table 4 shows the thicknesses of the phosphoric acid anodic coatings on the reproducibility panels anodized over a 9-month period and the corresponding concentration of the phosphoric acid in the anodizing bath, as determined by chemical titration. The bath concentration was the only variable that was not held to a specific value in this study, as it was allowed to vary within the 11-16 ounces per gallon concentration range given in the Boeing Process Specification. It is significant to note the dependence of the oxide thickness on the concentration of the anodizing bath, with higher bath concentrations producing a thicker oxide.

Figure 21 shows a plot of anodic film thickness as a function of the bath concentration for phosphoric acid anodizing of bare 7075-T6. The graph indicates that an increase in bath concentration of 2 ounces per gallon (from 12 to 14) results in a 30%

TABLE 4. REPRODUCIBILITY RESULTS ON PHOSPHORIC ACID ANODIZING OF BARE 7075-T6

ANODIZE DATE	AVERAGE OXIDE THICKNESS (Å)	BATH CONCENTRATION (oz/gallon)
5-14-75	3400	12.18
5-14-75	3700	12.18
6-4-75	3300	11.72
6-4-75	3300	11.72
6-4-75	3100	11.72
6-4-75	3000	11.72
6-16-75	2800	12.11
6-16-75	3200	12.11
6-16-75	2800	12.11
6-16-75	3200	12.11
7-15-75	3600	12.85
7-15-75	3600	12.85
7-15-75	3600	12.85
7-15-75	3600	12.85
7-16-75	4100	14.01
7-16-75	4100	14.01
8-11-75	4300	13.97
8-11-75	4100	13.97
8-14-75	4200	13.89
8-22-75	4200	13.92
8-28-75	4100	13.88
10-7-75	4000	13.98
11-11-75	3850	14.05
11-17-75	4150	14.01
11-19-75	4400	14.01
1-26-76	4100	14.03

increase in the anodic film thickness, or approximately 1000Å (from 3100Å to 4100Å). Due to the strong dependence of the anodic coating thickness on the bath concentration, it was decided to standardize the bath concentration at 14 ± 0.1 ounces per gallon.

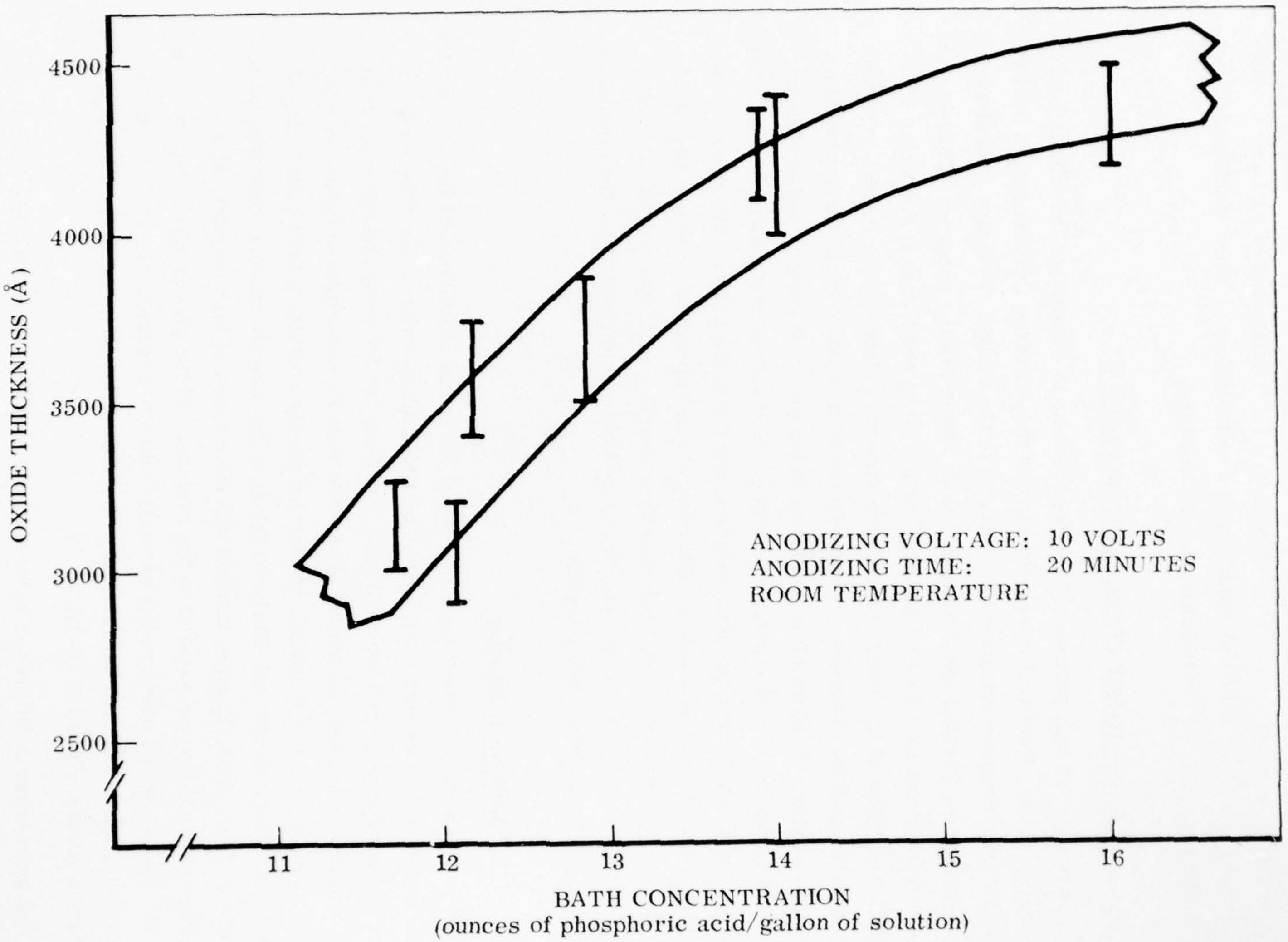


FIGURE 21. OXIDE THICKNESS ON BARE 7075-T6 VERSUS CONCENTRATION OF PHOSPHORIC ACID ANODIZING BATH

This concentration was then used as the standard for preparation of surfaces for adhesive bond evaluation, which included studies on the effect of other anodizing parameters on the character of the resulting anodic coatings.

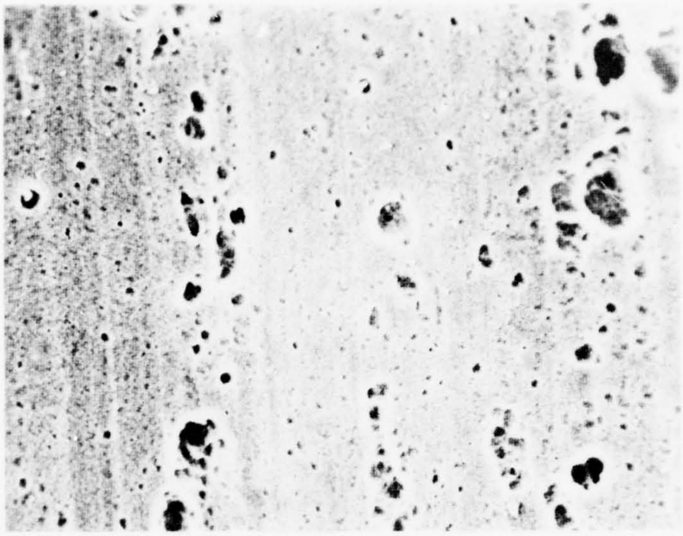
C. PHASE III – PABST COORDINATION STUDIES

The purpose of this portion of the program was to coordinate the efforts between McDonnell Douglas, Rockwell International, and the Northrop Corporation in the area of anodic surface characterization as it related to the PABST (Primary Adhesively Bonded Structures Technology) Program. Both Phase I of the program "Characterization of Surface Prior to Adhesive Bonding" at Northrop and Phase II conducted at Rockwell International Science Center, were directly related to the PABST program at McDonnell Douglas. Therefore, it was in the best interest of all three programs to have an exchange of information and ideas in the areas of anodic coating characterization and contamination of anodized surfaces. Northrop's assignment in this regard was to assure that all three programs were using the same anodic surfaces as a baseline and that the character of this anodic coating was reproducible over a period of time. This assignment was accomplished by conducting SEM characterization of panels taken from all three programs and by making comparisons with the standards established early in Northrop's program.

1. McDonnell Douglas

An arrangment was made with the PABST Program at McDonnell Douglas for the periodic inspection of production panels anodized in phosphoric acid. These panels were sectioned and prepared for SEM analysis using the 90° bend technique for specimen preparation. Figures 22 and 23 show SEM photomicrographs of typical anodic coatings taken from a set of PABST production panels containing both bare 2024-T3 and 7075-T6. Figures 22a and 23a were taken at low magnification (700X) normal to the surface plane, while Figures 22b and 23b were taken at high magnification (20,000X) along a direction parallel to the surface. These photographs, representing two of the four standard photographs normally taken to document the surface character of each panel, were selected because they show the differences in anodic coating character between 2024-T3 and 7075-T6.

The most cbvious difference between the anodized surfaces of 2024-T3 and 7075-T6 is the absence of grain boundary attack on the 2024-T3 surface. This etching of the grain boundaries occurs during the deoxidizing step, just prior to anodizing, and may be due to the differences in grain boundary constituents between the two



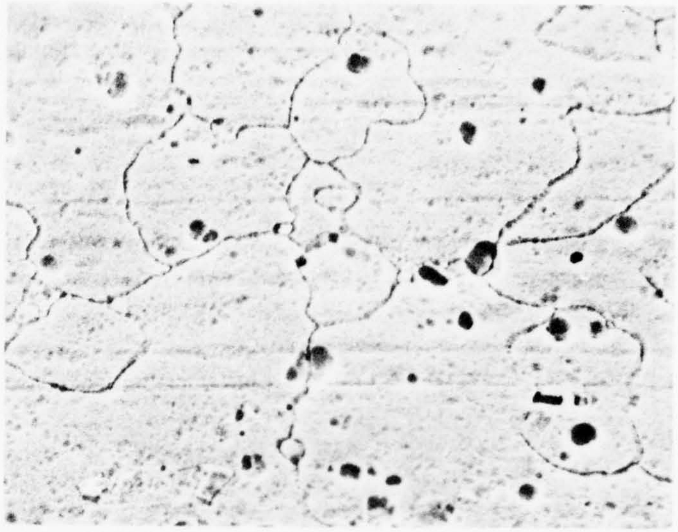
700X

a. NORMAL VIEW SHOWING LACK OF GRAIN BOUNDARY ETCHING

20, 000X

b. PARALLEL VIEW SHOWING OXIDE THICKNESS

FIGURE 22. ANODIZED SURFACE OF BARE 2024-T3 — PABST PRODUCTION PANEL



700X

a. NORMAL VIEW SHOWING GRAIN BOUNDARY ETCHING

20, 000X

b. PARALLEL VIEW SHOWING OXIDE THICKNESS

FIGURE 23. ANODIZED SURFACES OF BARE 7075-T6 — PABST PRODUCTION PANEL

alloys. The second difference between the phosphoric acid anodized surfaces of 2024-T3 and 7075-T6 is the thickness of the anodic coating. On the PABST production panels, the oxide coatings on 2024-T3 were found to be about 2200Å thick, whereas on 7075-T6, they were about 3500Å. This difference can be seen by comparing the oxide thickness of anodized bare 2024-T3, shown in Figure 22b, with that on bare 7075-T6, shown in Figure 23b. Other programs dealing with the anodizing of these alloys have shown similar results.(2)

The anodic coating thicknesses listed in Table 5 are from the PABST production panels of bare 2024-T3 and 7075-T6. They are listed in chronological order according to date received. These thicknesses were determined directly from SEM examination. The values compare favorably with specimens anodized under similar conditions both in this program and also in Phase II of this program at Rockwell International Science Center. Initially, the anodic film thicknesses on the PABST production panels were less than those produced by the standard phosphoric acid anodize used in this program. Panels received later in the program had coating thicknesses of the same magnitude as panels from this program.

In addition to the production panels, a series of laboratory specimens anodized in phosphoric acid under various conditions was submitted by McDonnell Douglas for examination and SEM characterization. These specimens were characterized and copies of all photomicrographs were submitted to McDonnell Douglas. Listed in Table 6 are the oxide thicknesses of these specimens, determined by SEM examination, as well as the anodizing conditions for each specimen. In general, these anodic coatings had thicknesses of the proper magnitude and were found to compare favorably with the PABST production panels in terms of physical character.

2. Rockwell Science Center

Included in this phase was the characterization of specimens of bare 7075-T6 anodized in phosphoric acid at Rockwell Science Center. The purpose of these specimens was to verify the existence of a properly anodized surface and to establish the anodic film character for use as a baseline surface in subsequent contamination studies at Rockwell Science Center. The SEM photomicrographs shown in Figures 24 and 25 are of the anodic coating on a typical specimen. The photograph in Figure 24, taken normal to the surface plane, shows the structure and porosity of the oxide layer. The anodic character shown in this photomicrograph compares favorably with panels anodized elsewhere under similar conditions, such as that shown in Figure 19. The thickness of the phosphoric acid anodic coating on the Rockwell panels of bare 7075-T6,

TABLE 5. ANODIC COATING THICKNESSES FROM PRODUCTION PANELS SUBMITTED BY McDONNELL DOUGLAS, PABST PROGRAM

DATE RECEIVED	AVERAGE OXIDE THICKNESS (Å)	
	BARE 7075-T6	BARE 2024-T3
6-30-75	3100	--
6-30-75	2900	--
6-30-75	2800	--
7-29-75	3600	1800
7-29-75	3400	1800
7-29-75	3500	1800
8-19-75	3700	3100
8-19-75	3800	2900
8-19-75	3600	3000
8-21-75	3900	2700
8-21-75	3700	3000
9-3-75	4500	3300
9-3-75	4600	3500
9-18-75	4700	3600
9-18-75	4200	3500

Production Anodizing Conditions:

10 volts
22.5 minutes

13.5 ounces of phosphoric acid/gallon of solution

78°F

as shown in Figure 25, was measured to be about 4000Å. This value also compares favorably to panels anodized elsewhere under similar conditions, with a typical one shown in Figure 20.

3. Surface Contamination

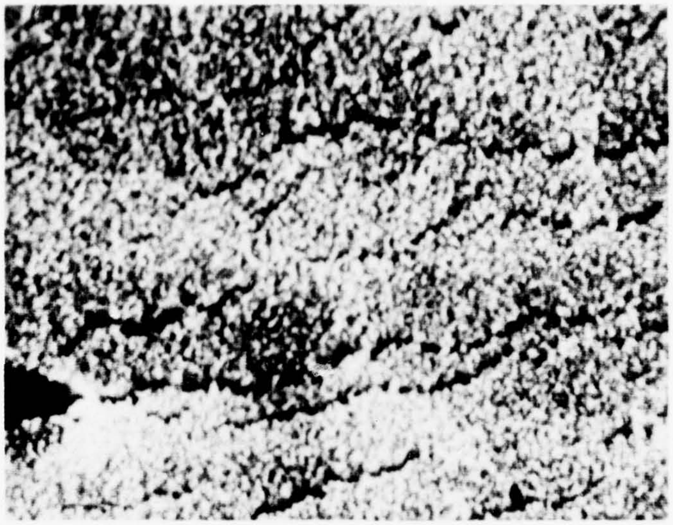
In general, it was found that all specimens submitted to Northrop for characterization in this phase exhibited surfaces of similar anodic film character. However,

TABLE 6. ANALYSIS OF LABORATORY SPECIMENS SUBMITTED BY McDONNELL DOUGLAS, PABST PROGRAM

SPECIMEN NUMBER	ALLOY	VOLTAGE (Volts)	BATH CONC. (oz/gal)	TEMP (°F)	TIME (min)	AVERAGE OXIDE THICKNESS (Å)
1	7075-T6	8	11	65	20	3300
3	7075-T6	8	11	65	25	4000
4	7075-T6	12	11	65	25	4200
10	7075-T6	10	13.5	78	22.5	4000
22	7075-T6	8	16	90	20	3400
25	7075-T6	12	16	90	25	4100
135	7075-T6	10	13.5	78	22.5	3800
9	2024-T3	10	13.5	78	22.5	4600
18	2024-T3	8	16	90	20	3300
21	2024-T3	12	16	90	25	4400
136	2024-T3	10	13.5	78	22.5	4700

some of the specimens received from the PABST Program had areas in which the anodic layer was either contaminated or damaged. The SEM photomicrograph in Figure 26 is typical of one of these areas and shows the oxide structure and porosity at 14,000X along a direction normal to the surface plane. The appearance of this oxide should have been similar to that shown in Figure 24. However, either abrasion or contamination had occurred from handling and storage of the panel in Kraft paper. This is evidenced by the smooth areas on the left- and right-hand sides of the etch pit in Figure 26.

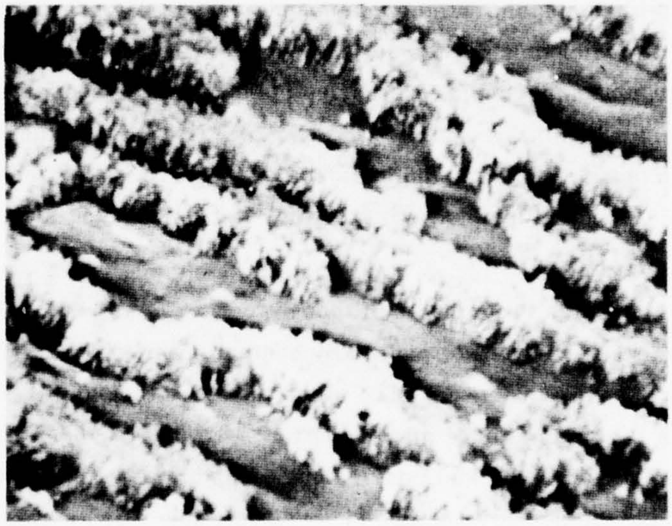
Presently, there are two schools of thought concerning these smooth-appearing areas. One is that these areas are caused by contamination from the Kraft paper which fills up the pores in the oxide. The other theory is that the Kraft paper abrades the anodic coating down to the bare metal. Extensive work has been performed in this area by the PABST Program at McDonnell Douglas and presently they favor the former theory.(3) That is, the abrasive nature of the anodic layer picks up some contamination (probably some form of carbon) from the Kraft paper. This results in a filling of the oxide pores by the contamination. In addition, it was demonstrated on the PABST Program that this type of surface condition was extremely detrimental to the durability of an adhesively bonded surface.



NORMAL
VIEW

14, 000X

FIGURE 24. CELL STRUCTURE ON BARE 7075-T6 — ROCKWELL SPECIMEN ANODIZED IN PHOSPHORIC ACID



PARALLEL
VIEW

17, 000X

FIGURE 25. OXIDE THICKNESS ON BARE 7075-T6 — ROCKWELL SPECIMEN ANODIZED IN PHOSPHORIC ACID

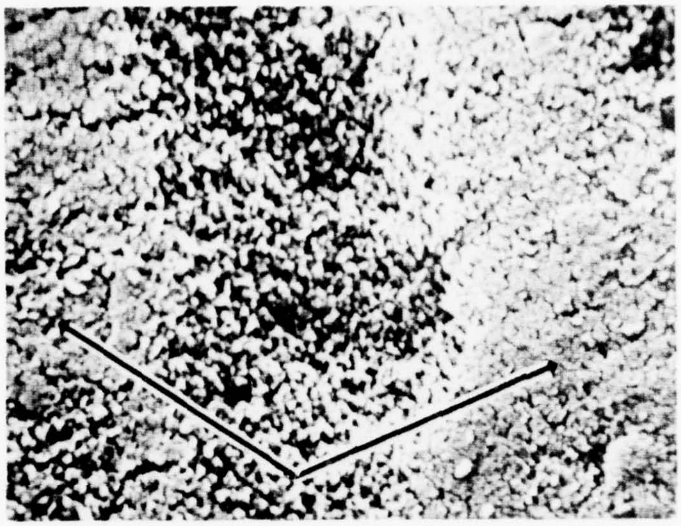


FIGURE 26. SURFACE OF BARE 7075-T6 — PABST PRODUCTION PANEL AFTER HANDLING WITH KRAFT PAPER

A short study was conducted in this program to substantiate the findings at McDonnell Douglas on the detrimental effect of Kraft paper handling (and cotton gloves) on the wedge test durability of a bonded surface. Wedge test panels were anodized in phosphoric acid using the standard conditions. The surfaces were then contaminated by handling with both Kraft paper and cotton gloves, by lightly rubbing them on the anodized surface and subsequently bonding them with FM-73 adhesive (no primer was used). A second set of specimens was prepared for SEM characterization of the contaminated anodized surface. No adhesive wedge test failures were noted after 24 hours of exposure; thus, the contaminated surfaces displayed acceptable durability behavior. Inspection of the contaminated surfaces in the SEM revealed a much lower amount of surface contamination coverage than was evidenced on the McDonnell Douglas panels, and this may have been the reason for the acceptable wedge test behavior of these panels. Substantial interest has been generated in this area of contamination by handling with Kraft paper and cotton gloves, and further studies are necessary in this area.

A formal presentation was made of the progress on this program at the PABST Roadmap and Coordination Session held at McDonnell Douglas in Long Beach on 8 October 1975.

D. PHASE IV – ADHESIVE BOND DURABILITY OF ANODIZED SURFACES

In this portion of the program, the adhesive bond durability of anodized surfaces was correlated with the character of the surfaces as determined by SEM inspection prior to bonding. The work was divided and conducted in two distinct, but interrelated tasks. The first task involved determining the effect of changes in the anodizing conditions on the character of the resulting anodic film. The character of the anodized surfaces was determined by SEM examination and documented with standard SEM photomicrographs. The second task involved determining the effect of changes in the anodizing conditions on the environmental durability of the anodized surfaces as determined by wedge testing. The selection of the anodizing conditions for durability evaluation was based on the characterization results from the first task.

The anodizing parameters selected were those considered most likely to change in a production anodizing environment. These parameters included:

1. Pretreatment prior to anodizing
2. Rate of initial application of anodizing voltage
3. Anodizing voltage
4. Anodizing time
5. Anodizing bath concentration
6. Panel spacing during anodizing
7. Time interval between anodizing and rinsing.

The effect of the anodizing parameters on the character of the anodic coatings was determined by varying each parameter, one at a time, from its standard value, while holding all other parameters at standard conditions. SEM inspection and documentation of the resulting anodic surfaces were performed and a correlation was made between the changes in the anodizing conditions and the resulting surface character. Based on these results, a limited number of panels, 6-inch by 6-inch by 0.125-inch, were anodized using the conditions which yield the desired surface characteristics. These panels were adhesively bonded with FM-73 (no primer was used) and wedge tested to determine the durability of the anodic surface. The primer was omitted to provide a more sensitive measure of the durability as a function of anodic film character.

1. Wedge Test Procedure

The wedge testing procedures were based on the Boeing Process Specification, BAC-5514, with the configuration of the standard wedge panel shown in Figure 27. The

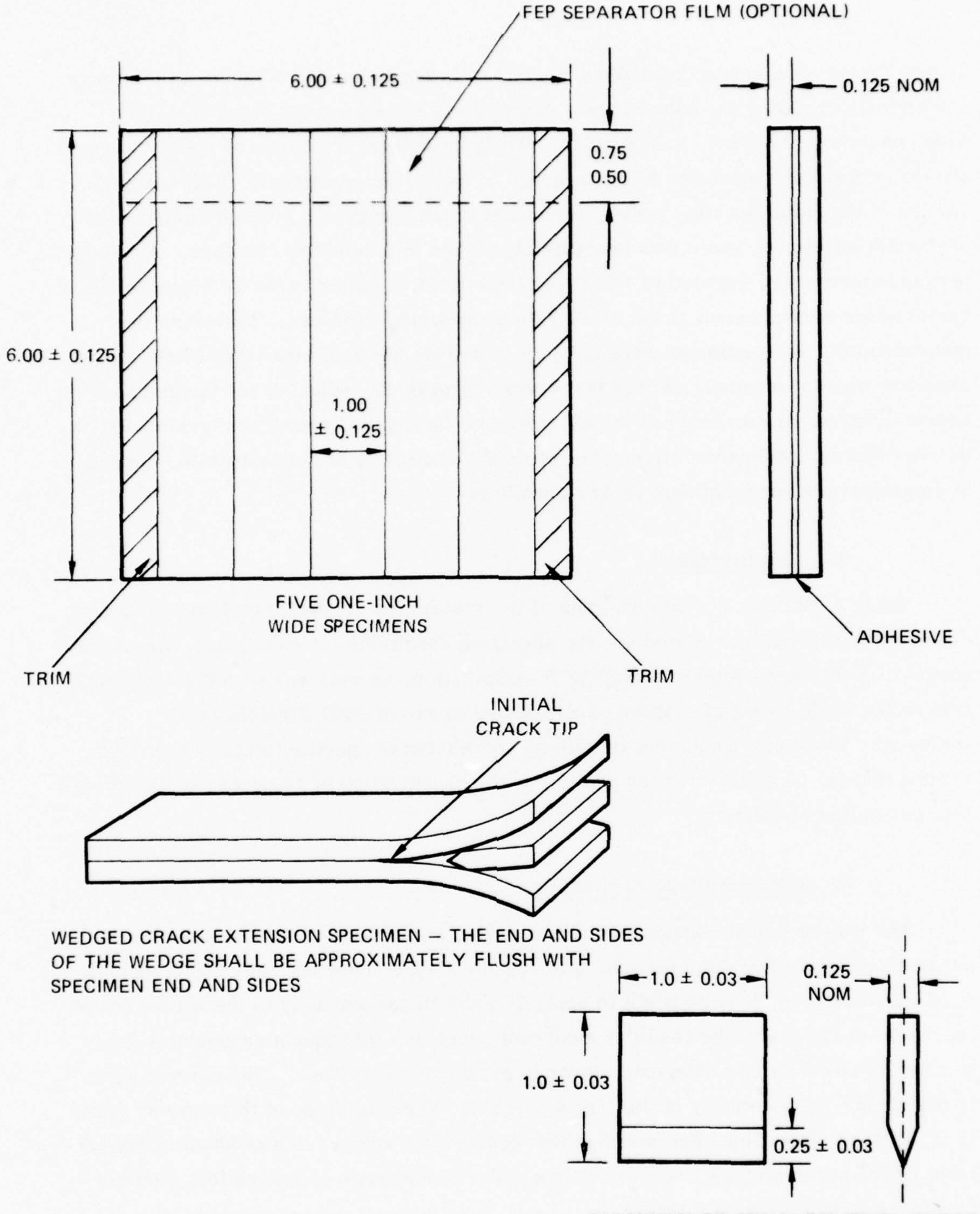


FIGURE 27. STANDARD WEDGE TEST PANEL AND COUPON

6-inch square panels were anodized and adhesively bonded within 24 hours to minimize contamination. After the adhesive was cured, the panels were cut into five 1-inch wide specimens, as shown in Figure 27. Wedge test data for one set of anodizing conditions is normally presented as the average of these five specimens. Following insertion of the stainless steel wedge, the initial crack length was scribed on the sides of the test specimen, and it was immediately placed in a humidity chamber. All wedge test specimens were exposed to 120°F and 100% relative humidity for 24 hours and then removed for measurement of the crack extension during exposure. Following this measurement, the specimens were split apart and the mode of crack extension during exposure was documented. Wedge test cracks through the adhesive are termed cohesive failures, cracks between the adhesive and the anodic coating are termed adhesive failures. Adhesive failures are generally indicative of poor durability caused by improper surface treatment prior to bonding.

2. Test Results

Table 7 contains a summarization of the results for all wedge test specimens evaluated in this phase. Listed are the anodizing conditions for each panel, the average anodic film thickness determined by SEM examination, as well as the wedge test crack growth and mode results for those panels whose environmental durability was evaluated. Values for anodizing conditions not otherwise specified were at standard values; that is, 10 volts, 20 minutes, in a bath concentration of 14 ounces of phosphoric acid per gallon of solution.

3. Rate of Voltage Application

The rate of initial voltage application during an anodizing run is an important parameter in the anodizing process. In laboratory-type anodizing runs with panels of small surface area, it is possible to apply 10 volts instantaneously to the specimens at the outset of the run. The result is a current surge and subsequent exponential decay to a steady-state value as the oxide layer is grown on the surface. The current surge is due to the low resistivity of the virgin surface. The magnitude of this current spike is often 10 or more times greater than the steady-state value. In a production environment where panel surface areas are on the order of hundreds of square feet (compared to a few square inches on a laboratory panel), it is difficult to accommodate these high current surges at the outset of the anodizing run. Thus, a gradual application of the initial anodizing potential is highly desirable.

TABLE 7. SUMMARIZATION OF ANODIC SURFACE CHARACTER AND WEDGE TEST RESULTS

ANODIZING CONDITIONS*	AVERAGE ANODIC FILM** THICKNESS (Å)	CRACK GROWTH*** (INCHES)	ESTIMATED*** % COHESIVE FAILURE
Rate of Voltage Application			
Gradual (2 min. to full voltage)	3900	0.12	100
Gradual (2 min. to full voltage)	4100	0.15	90
Gradual (2 min. to full voltage)	4000	0.16	100
Instantaneous Voltage	4000	0.13	100
Instantaneous Voltage	4400	0.16	95
Instantaneous Voltage	4100	0.13	100
Anodizing Time			
1 minute	800	1.98	0
2 minutes	1400	0.15	5
4 minutes	2000	0.18	0
5 minutes	2900	0.19	75
7 minutes	3700	0.14	90
8 minutes	3800	0.10	90
10 minutes	4100	--	--
15 minutes	4200	--	--
20 minutes	4300	0.13	100
25 minutes	4400	--	--
30 minutes	4800	0.13	70
Anodizing Voltage			
1 volt	500	2.23	0
3 volts	1200	0.13	35
5 volts	1900	0.17	80
8 volts	2900	0.18	90
10 volts	4100	0.13	100
12 volts	4800	--	--
15 volts	6600	0.16	95
Anodizing Voltage and Time			
5 volts, 7 minutes	1900	0.16	75
7 volts, 7 minutes	2500	0.14	80
Surface Pretreatment			
Degreased, alkaline cleaned, anodized	5000	0.19	90
Degreased, anodized	4800	0.15	90

---

* All conditions are standard unless otherwise noted: 10 volts, 20 minutes and 14 ounces/gallon.

** Determined through SEM examination.

*** Average result for 5 specimens. Exposed to 120°F and 100% RH for 24 hours.

TABLE 7. SUMMARIZATION OF ANODIC SURFACE CHARACTER AND WEDGE TEST RESULTS (Continued)

ANODIZING CONDITIONS*	AVERAGE ANODIC FILM** THICKNESS (Å)	CRACK GROWTH*** (INCHES)	ESTIMATED*** % COHESIVE FAILURE
Specimen Arrangement During Anodizing			
0-inch panel spacing	1300	--	--
0.125-inch panel spacing	3800	0.14	80
0.250-inch panel spacing	4000	--	--
0.375-inch panel spacing	4200	--	--
Shelf-Life Evaluation			
24-day exposure to air prior to bonding	4100	0.11	95
No Anodize			
Zero volts (in bath for 20 min.)	0	2.70	0
Degreased, alkaline cleaned, deoxidized	0	2.88	0
Bath Concentration			
11 oz/gal	3200	0.12	85
16 oz/gal	4300	0.13	100
Post Anodize Handling			
1 min. in bath before rinse	3700	--	--
2 min. in bath before rinse	3000	0.16	100
5 min. in bath before rinse	2000	--	--
10 min. in bath before rinse	1100	2.90	0

---

[*] All conditions are standard unless otherwise noted: 10 volts, 20 minutes and 14 ounces/gallon.

[**] Determined through SEM examination.

[***] Average result for 5 specimens. Exposed to 120°F and 100% RH for 24 hours.

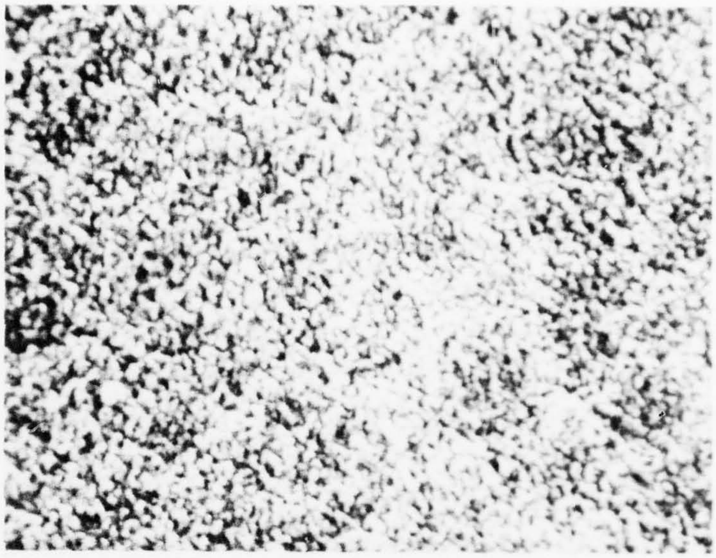
The differences in oxide character resulting from instantaneous versus gradual voltage application were studied through SEM characterization and wedge test durability evaluation of the anodic coatings. A comparison of the cell structure and porosity of the anodic coatings resulting from instantaneous and gradual voltage application is shown in the SEM photomicrographs of Figure 28. As is seen in these photographs, the differences in oxide character are barely detectable, with the gradual voltage application producing a slightly finer cell structure. Subsequent wedge testing showed no difference in the durability between gradual and instantaneous voltage application techniques, as shown in Table 7.

4. Anodizing Time

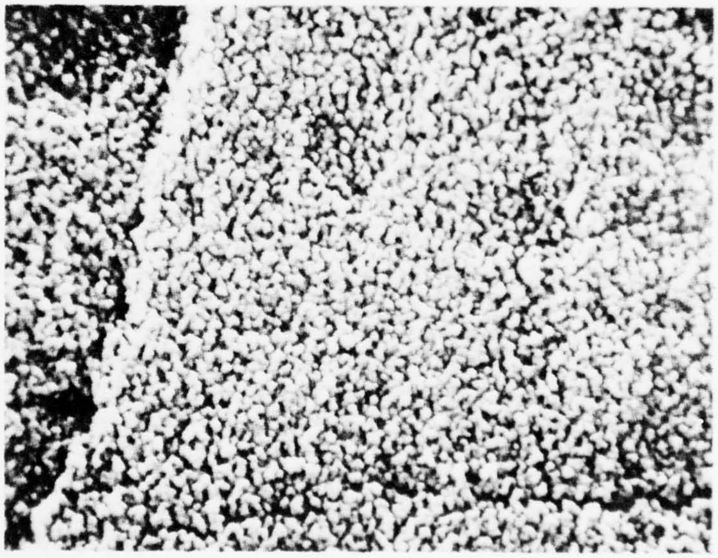
The effect of anodizing time on the thickness of the anodic coating formed by the phosphoric acid anodizing of bare 7075-T6 was studied in this phase. Specimens were anodized for times varying from one minute to thirty minutes at 10 volts in a bath concentration of 14 ounces per gallon. The resulting anodized surfaces were characterized with the SEM. The anodic coating thicknesses for these specimens are listed in Table 7. A plot of these results, as shown in Figure 29, reveals the parabolic dependence of anodic coating thickness on anodizing time. The growth rate decreases with time and an oxide thickness of 4000Å is achieved in about ten minutes and a thickness of only 4500A is achieved after thirty minutes. The Boeing Process Specification specifies a 20-25 minute anodizing time, which is well into the plateau region of the curve.

High magnification SEM inspection of the anodic film character as a function of anodizing time revealed the development of the oxide, as shown in Figure 30. These photomicrographs, taken at the magnification of 14,000X, compare the surfaces of specimens anodized for 1, 4, 7, 10, 20, and 30 minutes. They show the development of the oxide cell structure and size as a function of anodizing time. The SEM photomicrograph shown in Figure 30 indicates that cell size increases with anodizing time, reaching a growth plateau after about 15 minutes.

Wedge testing of the specimens anodized for various lengths of time revealed a direct correlation between anodic coating character and wedge test durability. Figure 31 compares the wedge test fracture surfaces after exposure which correspond to the oxide surfaces shown in Figure 30. Each specimen is typical of the mode of failure for the anodizing conditions tested. The specimens are shown after exposure and splitting. The one and four-minute anodize specimens, with surfaces as shown in Figures 30a and 30b, exhibited an unacceptable wedge test behavior. Wedge testing



a. GRADUAL VOLTAGE APPLICATION



b. INSTANTANEOUS VOLTAGE APPLICATION

FIGURE 28. EFFECT OF RATE OF VOLTAGE APPLICATION ON THE OXIDE CELL STRUCTURE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

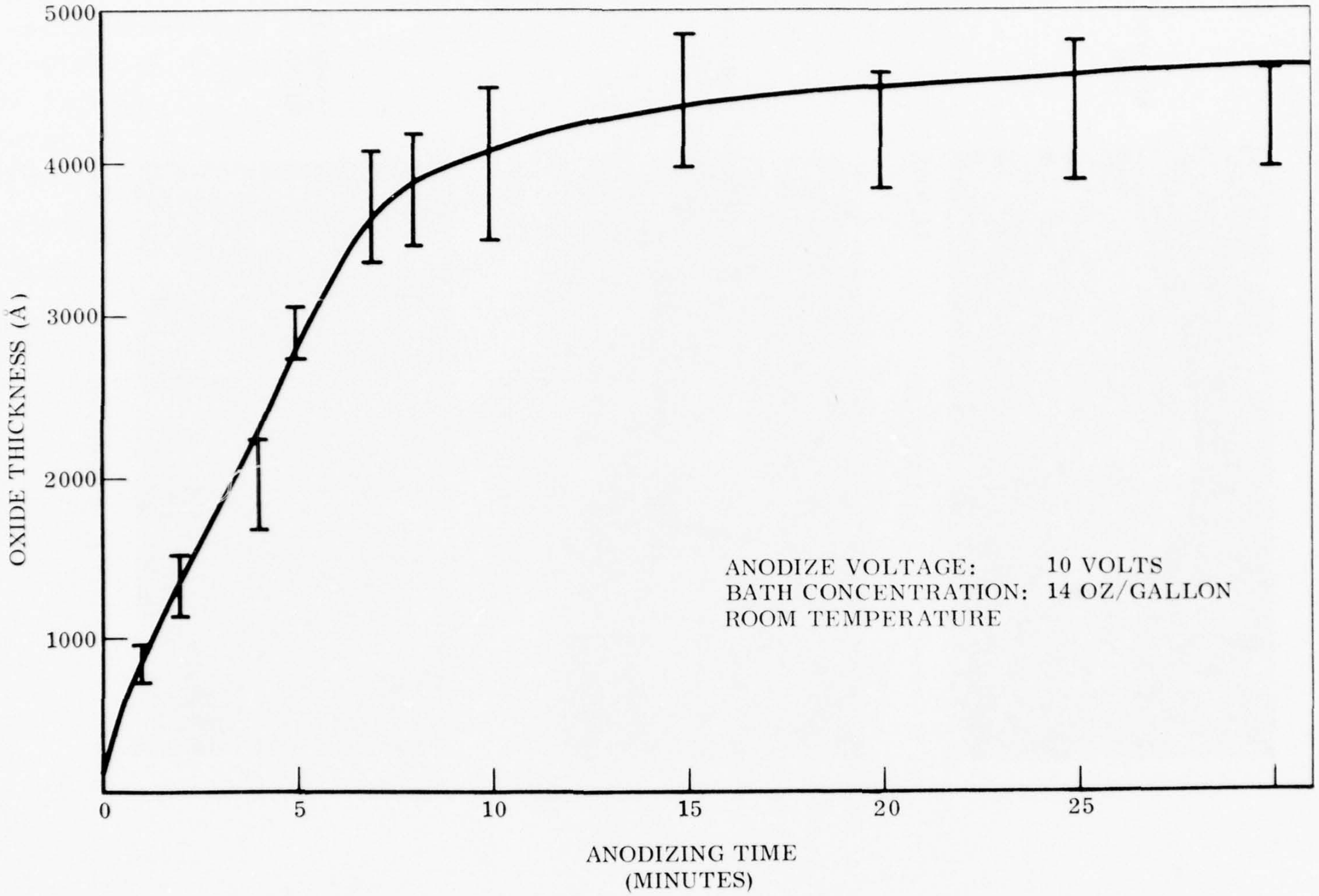
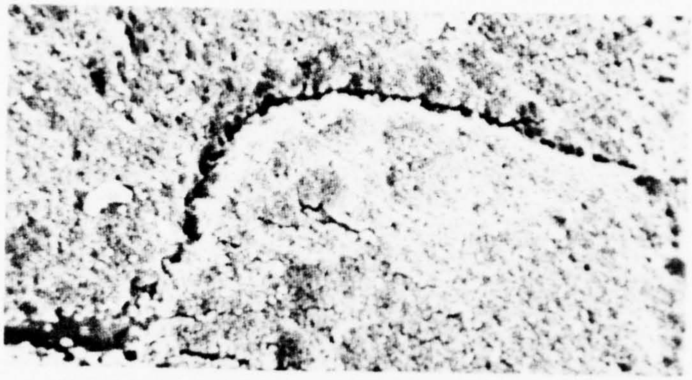
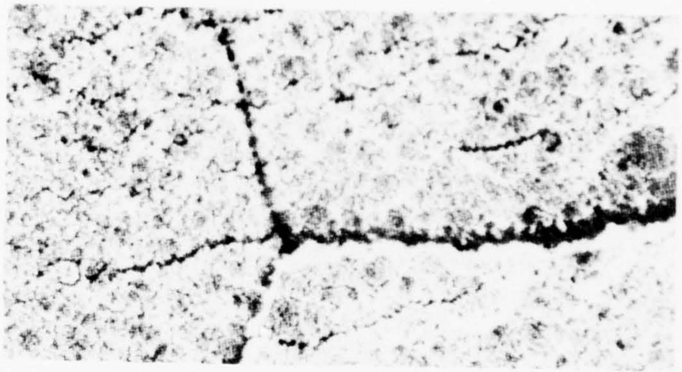


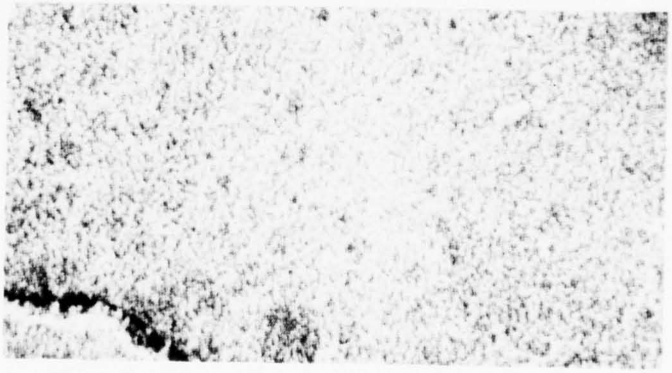
FIGURE 29. OXIDE THICKNESS VERSUS ANODIZING TIME FOR BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



a. 1 MINUTE 14,000X

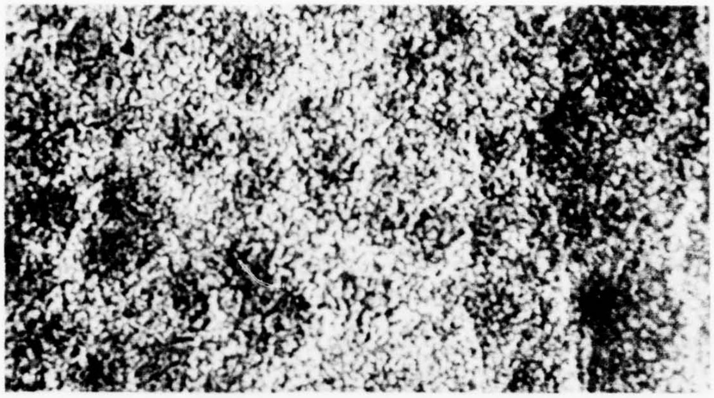


b. 4 MINUTES 14,000X



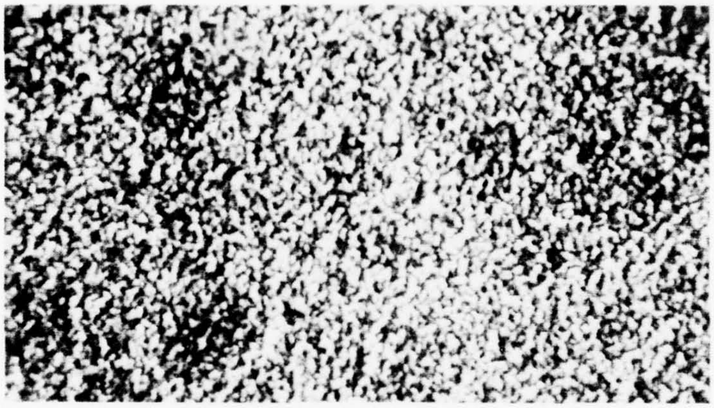
c. 7 MINUTES 14,000X

FIGURE 30. EFFECT OF ANODIZING TIME ON OXIDE CELL STRUCTURE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



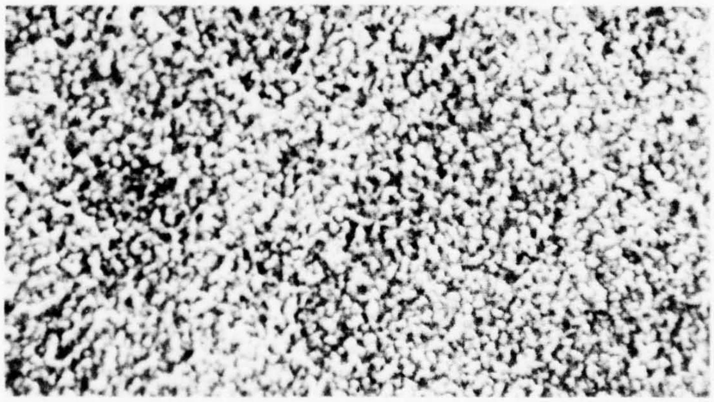
NORMAL VIEW

d. 10 MINUTES 14, 000X



NORMAL VIEW

e. 20 MINUTES 14, 000X



NORMAL VIEW

f. 30 MINUTES 14, 000X

FIGURE 30. EFFECT OF ANODIZING TIME ON OXIDE CELL STRUCTURE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID (Continued)

of the one minute anodize resulted in a crack growth of nearly two inches in an adhesive manner, as shown in Figure 31. The four-minute anodize wedge test exhibited nominal crack growth (0.18-inch); however, the crack grew in an adhesive manner. This is not optimum from a durability standpoint. The seven-minute anodize, producing the surface character shown in Figure 30c, exhibited acceptable crack growth and mode. To allow for a margin of safety, the SEM photomicrograph shown in Figure 30d of the ten-minute anodize was selected as showing the lower limit of acceptability of cell structure and size for a durable anodized surface. Thus, during the SEM inspection procedure, surfaces exhibiting a less developed cell structure than that shown in Figure 30d would be rejected. This includes surfaces similar to those shown in Figures 30a-c.

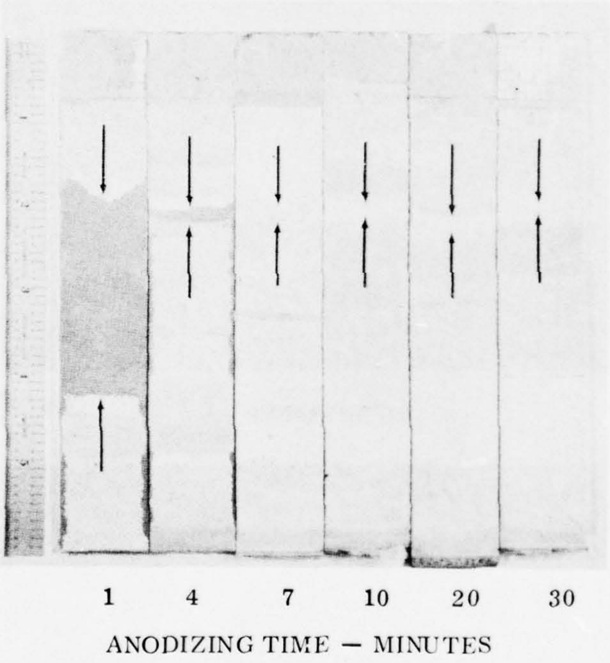


FIGURE 31. WEDGE TEST BEHAVIOR VERSUS ANODIZING TIME

5. Anodizing Voltage

The effect of anodizing voltage on the oxide character and subsequent wedge test durability was evaluated to determine the sensitivity of the SEM in detecting changes in the surface character due to voltage changes. Specimens were anodized at voltages varying from 1 volt to 15 volts for 20 minutes in a bath concentration of 14 ounces per gallon. The thicknesses of these coatings were determined as a function of anodizing voltage as shown in Table 7. A plot of these results, as shown in Figure 32, indicates a linear-relationship between anodic film thickness and anodizing voltage. The oxide thickness increased at the rate of 420Å per volt in these tests.

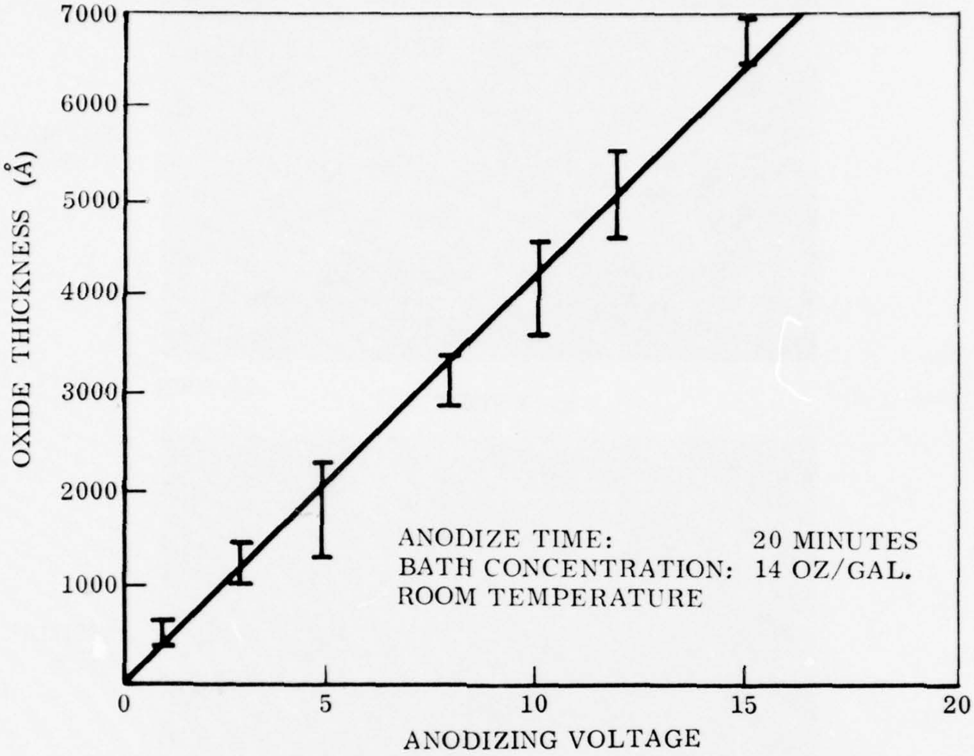
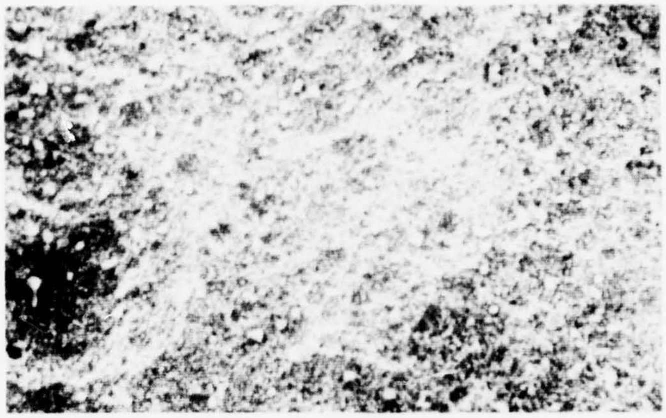


FIGURE 32. OXIDE THICKNESS VERSUS ANODIZING VOLTAGE FOR BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

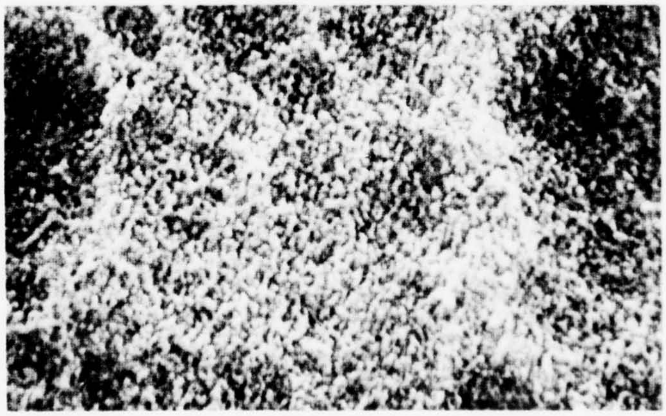
The cell structures of these anodic coatings were examined at high magnification and show a dependence of cell size on anodizing voltage. Figure 33 compares the cell size of specimens anodized at 1, 3, 5, 8, 10, and 15 volts. The differences in cell size and structure are quite evident, with the cell size increasing as the voltage increases.

The durability evaluation of the surfaces which were anodized at various voltages provided a correlation between anodic surface character and wedge test behavior. Panels were anodized at 1, 3, 5, 8, 10, and 15 volts, bonded with FM-73 adhesive, and evaluated by wedge testing. Figure 34 shows the fracture surfaces of typical specimens from each of the six panels after wedge test exposure. The arrows indicate the extent of crack growth. The wedge test behavior of the one-volt anodize, with surface character shown in Figure 33a, was similar to that of the one-minute anodize discussed earlier, with over two inches of adhesive crack growth occurring



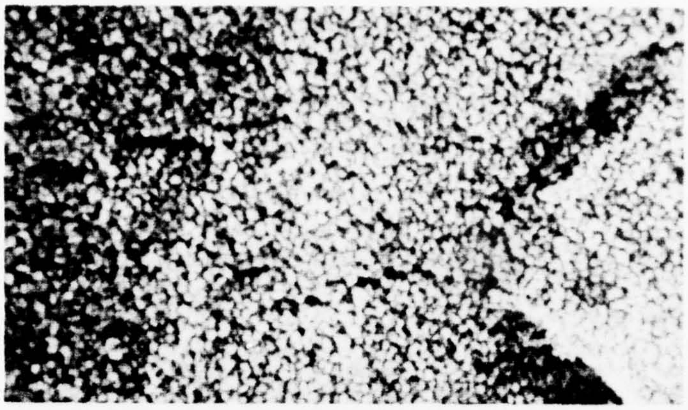
a. 1 VOLT

b. 3 VOLTS



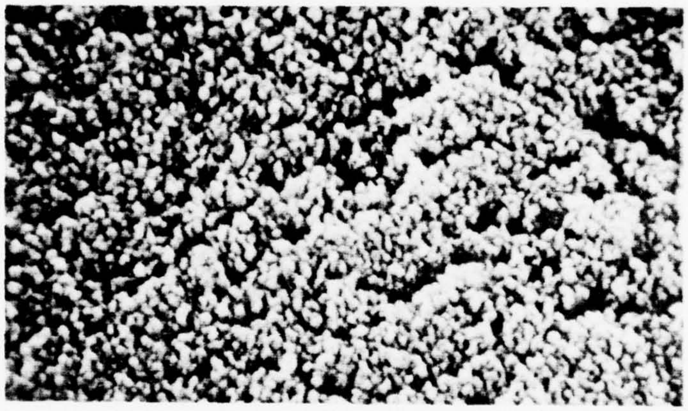
c. 5 VOLTS

FIGURE 33. EFFECT OF VOLTAGE ON OXIDE CELL STRUCTURE ON BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



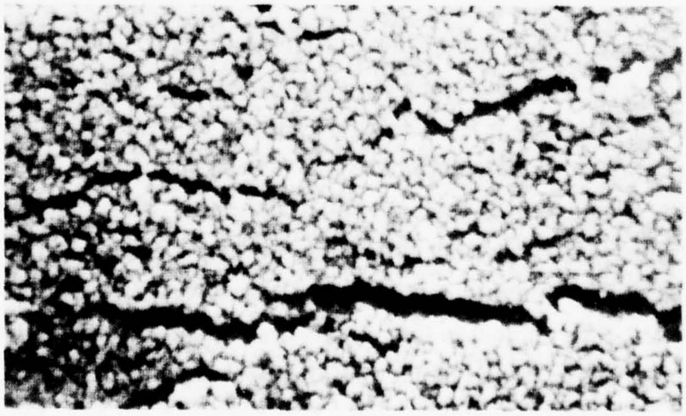
14,000X

d. 8 VOLTS



14,000X

e. 10 VOLTS



14,000X

f. 15 VOLTS

FIGURE 33. EFFECT OF VOLTAGE ON OXIDE CELL STRUCTURE ON BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID (Continued)

during the exposure. The three-volt anodize, with the surface character shown in Figure 33b, exhibited acceptable wedge test crack growth; however, the majority of the growth was in an adhesive manner. The five-volt anodize with a more highly developed cell structure, as shown in Figure 33c, exhibited acceptable wedge test durability behavior, as shown in Figure 34.

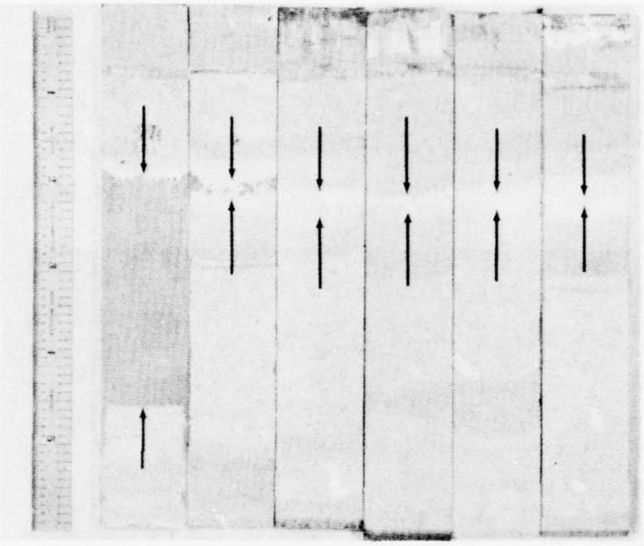


FIGURE 34. WEDGE TEST BEHAVIOR VERSUS ANODIZING VOLTAGE

The durability results shown in Table VII indicate that a 2000Å thick coating, provided by anodizing for four minutes at ten volts, exhibited unacceptable wedge test behavior; whereas, a 1900Å thick coating, achieved by anodizing at five volts for twenty minutes, exhibited acceptable behavior. Despite the nearly equivalent oxide thicknesses, a comparison of the oxide coating on the two surfaces, shown in Figures 30b and 33c, reveals a distinct difference in the oxide structure. Anodizing at five volts produced a more highly developed cell structure and formed a more uniform oxide coating. This indicates that durability depends on more than the anodic coating thickness. However, it was found that all specimens having an oxide thickness of 3000Å or greater exhibited acceptable wedge test behavior. Thus, for the SEM inspection procedure, a conservative lower limit on oxide thickness was set at 3000Å for acceptance of a surface that will yield a durable adhesive bond.

6. Anodizing Voltage and Time

Both anodizing time and voltage were varied on two test panels to verify the acceptance limits established for the cell structure and thickness of the anodic coating. Panels of bare 7075-T6 were anodized at 5 and 7 volts for seven minutes in a bath concentration of 14 ounces per gallon, bonded with FM-73 adhesive, and wedge tested. Figures 35 and 36 show the cell structure of the anodic coatings on these specimens. These anodized surfaces are similar in terms of cell size to the 3-volt, 20-minute anodize surface shown in Figure 33b. According to the acceptance criteria established, both panels would be rejected due to insufficient oxide cell development. The thickness of the anodic coating resulting from the 5-volt, 7-minute anodize, was measured to be 1900Å and the 7-volt, 7-minute anodize had an anodic coating thickness of 2500Å. Using the 3000Å minimum oxide thickness criteria, both panels would be rejected. Wedge tests of these panels exhibited marginally acceptable durability (Table 7), indicating that the 3000Å standard provides a margin of safety.

7. Panel Pretreatment

The effect of improper pretreatment on the resulting anodic film character and durability was evaluated. The objective was to determine whether the effects of improper pretreatment processing could be detected through examination of the final anodic surface coatings. Three sets of specimens were made. The first set was vapor degreased and anodized, the second set was vapor degreased, alkaline cleaned, and anodized, and the third set was given the full pretreatment processing (including deoxidizing), and anodized.

Examination of the resultant anodic films with the SEM showed that the oxide thicknesses of those specimens that were improperly pretreated was greater than those which were properly pretreated. Specimens that were only degreased prior to anodizing had an oxide thickness which averaged about 5000Å; specimens that were degreased and alkaline cleaned had an average oxide thickness of about 4800Å; and properly pretreated specimens had an average oxide thickness of about 4200Å. The difference in thicknesses is probably due to the incomplete removal of the residual oxide from the surface by improper pretreatment. The residual oxide acts as a base for anodic oxide growth and results in a total oxide layer which is thicker than normal.

Further SEM examination of the improperly pretreated surfaces revealed differences in the extent of grain boundary attack between specimens that were and were

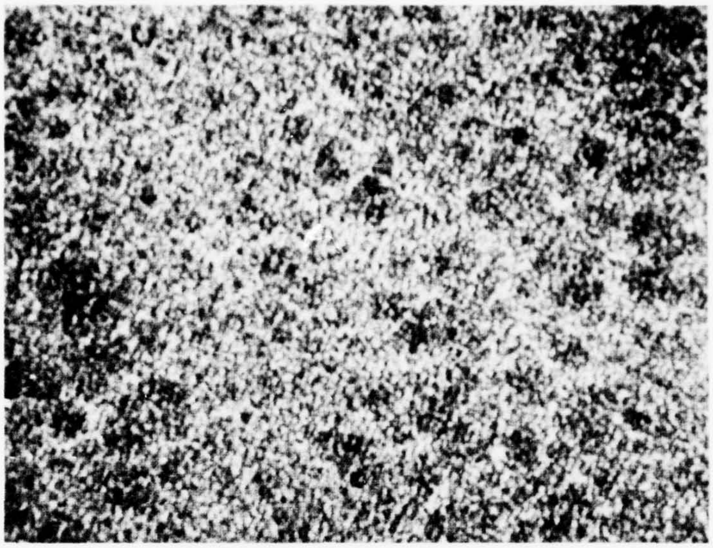


FIGURE 35. OXIDE CELL STRUCTURE FOR 5-VOLT, 7-MINUTE PHOSPHORIC ACID ANODIZING OF BARE 7075-T6

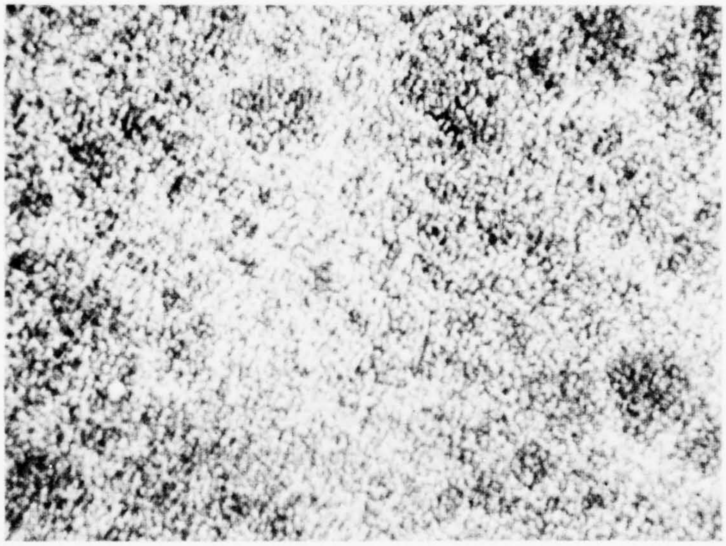


FIGURE 36. OXIDE CELL STRUCTURE FOR 7-VOLT, 7-MINUTE PHOSPHORIC ACID ANODIZING OF BARE 7075-T6

not properly pretreated. Little or no grain boundary etching occurred in those specimens that were not deoxidized prior to anodizing. This effect is seen by comparing the surfaces of the three sets of specimens, as shown in Figure 37. These show that SEM examination of an anodized surface is a viable method to determine whether or not the surface has been properly deoxidized prior to anodizing.

Wedge testing results in Table 7, for specimens that were improperly pretreated prior to anodizing show that despite the omission of the deoxidizing step no detrimental effect is seen on the wedge test durability of these specimens. Both pretreatments exhibited nominal crack growth (0.15 to 0.19-inch) in an almost completely cohesive manner. This result was unexpected, since it is known that the residual oxide layer on the as-received aluminum is of the bayerite form, which is the weakest link in the adhesive-metal interface.

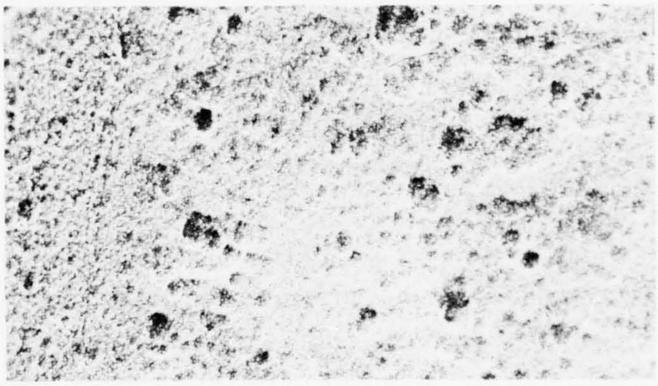
There are two possible explanations for the fact that the panels, which were anodized after an improper pretreatment, had a thicker oxide coating and exhibited acceptable wedge test durability. The first, is that during the phosphoric acid anodizing of a surface which has a residual layer of bayerite, the combination of the acid electrolyte and the anodizing potential results in the conversion of the bayerite layer to boehmite. This would occur prior to, or during, the formation of the boehmite anodic layer. The second, and vastly different explanation, is that anodizing a panel having a residual bayerite layer on the surface forms a stratified oxide coating, with boehmite forming on top of the bayerite. During the wedge test of this stratified oxide surface, the boehmite layer acts as a protective barrier, preventing moisture from reaching the underlying bayerite oxide at least for the exposure times involved. Without the presence of moisture, the bayerite layer cannot grow, at the expense of the boehmite layer, to a size that would result in failure of the metal-oxide interface.

Despite the results that indicate that proper deoxidizing may not be critical to the formation of a durable surface, it was decided that any phosphoric acid anodized surface on bare 7075-T6 which does not show some grain boundary attack should be rejected. Thus, any surface not comparable to the surface shown in Figure 37c at 2800X should be rejected.

8. Panel Spacing During Anodization

Panel spacing was another anodizing variable which was evaluated in this phase of the program. It was designed to evaluate the throwing power and shadowing effects that might occur during the anodizing process. Pairs of 6-inch by 6-inch wedge test

a. VAPOR DEGREASED, ANODIZED



b. VAPOR DEGREASED. ALKALINE CLEANED, ANODIZED

c. VAPOR DEGREASED, ALKALINE CLEANED, DEOXIDIZED, ANODIZED

FIGURE 37. EFFECT OF SURFACE PRETREATMENT ON GRAIN BOUNDARY ETCHING — BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

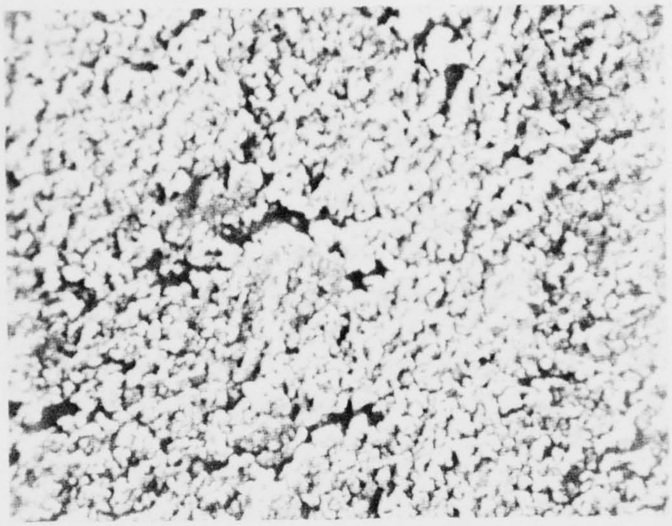
panels were spaced 0, 0.125, 0.250, and 0.375-inch apart, fastened together with aluminum wire, and given the standard pretreatment and anodizing procedures. SEM characterization of the resulting surfaces revealed that a zero specimen spacing was inadequate for proper anodizing. As seen in the SEM photomicrographs in Figures 38a and 39a, the zero-spacing panels still resemble an as-received surface covered with residual oxide. During the pretreatment and anodizing processes, these panels were in contact with each other. This prohibited the various solutions from reaching the surface, which resulted in little change of the as-received surface. On the other hand, the 0.125-inch spaced panel, with a width to spacing ratio of 24:1, had acceptable anodic film character, as shown in Figures 38b and 39b. Wedge test evaluations of two 6-inch square panels spaced 1/8-inch apart during anodizing resulted in acceptable durability for these surfaces, as listed in Table 7.

9. Omission of Anodize

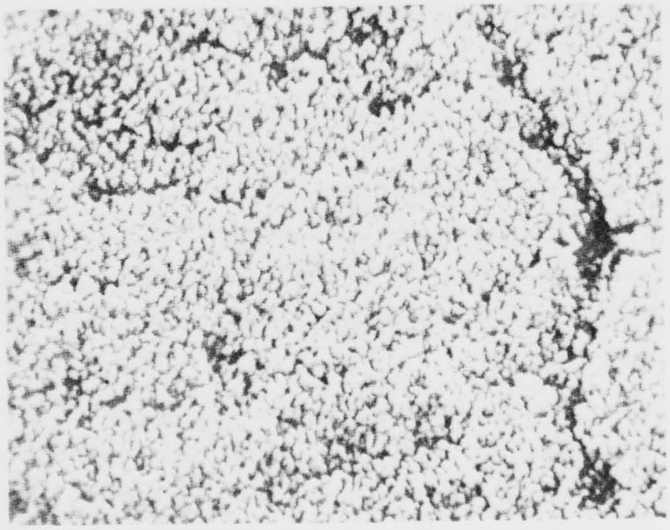
One step which may not be omitted from this procedure is that of the anodizing process itself. Two instances which might occur in a production environment are: (1) the panel may completely miss the anodizing step or (2) the panel may be placed in the anodizing tank for 20 minutes with no voltage applied. In either case, the SEM inspection procedure must be able to identify and single out these two types of anodizing errors.

Two groups of bare 7075-T6 specimens were used for this test. The first group was pretreated according to specification and then rinsed and oven dried (completely omitting the anodizing process). These are referred to as the deoxidized panels. The second was pretreated, then immersed in the anodizing bath for 20 minutes with no potential applied, followed by removal for rinsing and drying. The surfaces of one panel from each group was characterized with the SEM, and the other panels were bonded for durability evaluation.

The character of a deoxidized panel surface is shown in the SEM photomicrographs of Figure 40. These photographs, when compared to similar photographs of an anodized surface, show the differences between a deoxidized and an anodized surface. A comparison of Figure 40a with that of the standard anodize shown in Figure 8a shows the complete absence of a porous anodic layer on the deoxidized surface. In comparing the thickness of the oxide layer on the deoxidized surface shown in Figure 40b with that on the standard anodize shown in Figure 9a, it is evident that no anodic coating is present on the surface. Wedge testing showed

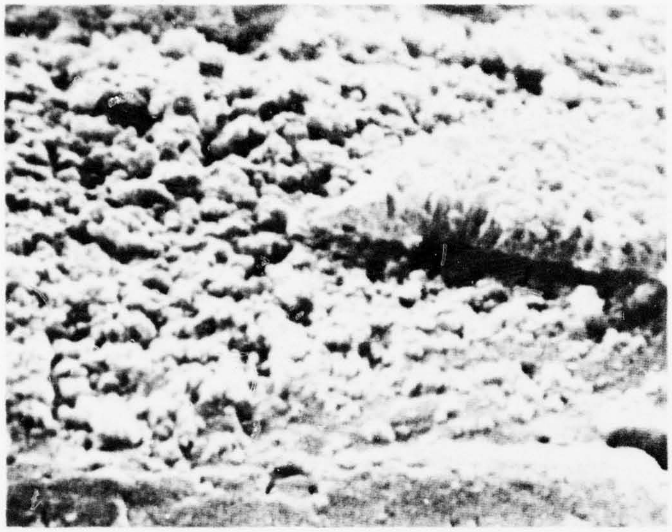


a. ZERO-INCH SPECIMEN SPACING



b. 0.125-INCH SPECIMEN SPACING

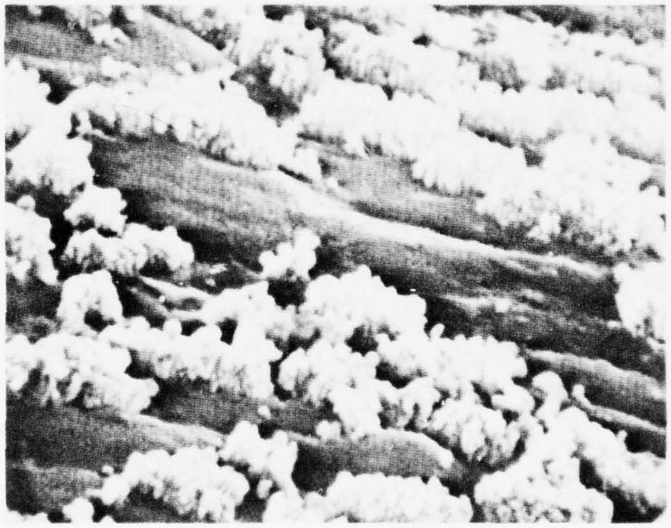
FIGURE 38. EFFECT OF SPECIMEN SPACING ON CELL DEVELOPMENT — BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



PARALLEL
VIEW

20,000X

a. ZERO-INCH SPECIMEN SPACING

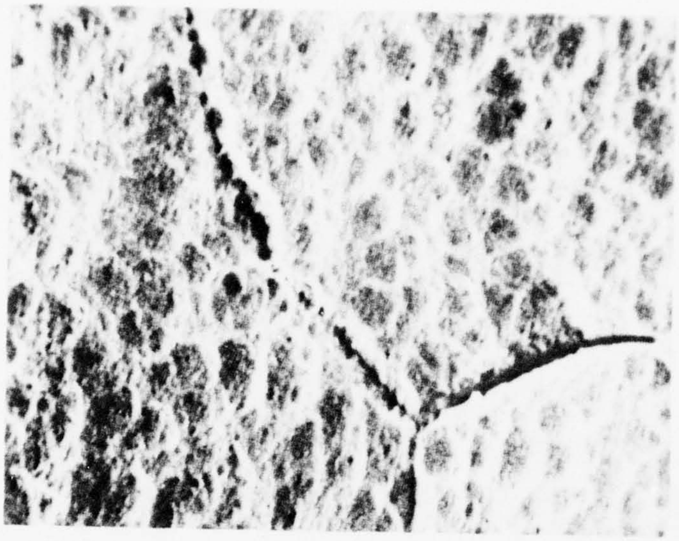


PARALLEL
VIEW

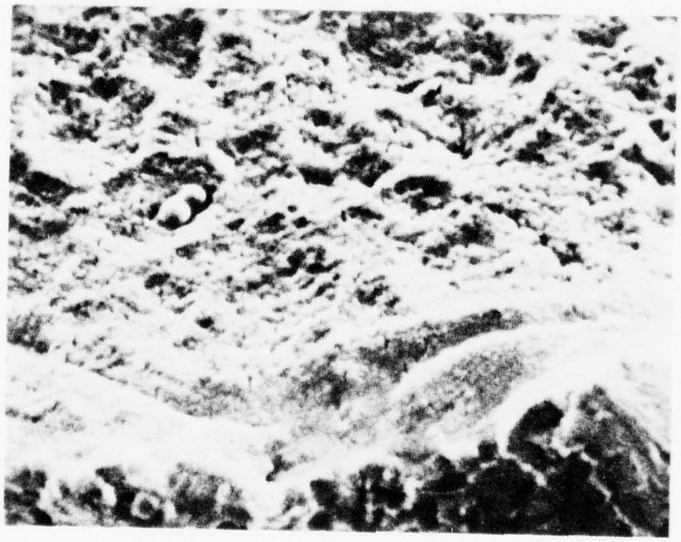
20,000X

b. 0.125-INCH SPECIMEN SPACING

FIGURE 39. EFFECT OF SPECIMEN SPACING ON OXIDE THICKNESS — BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



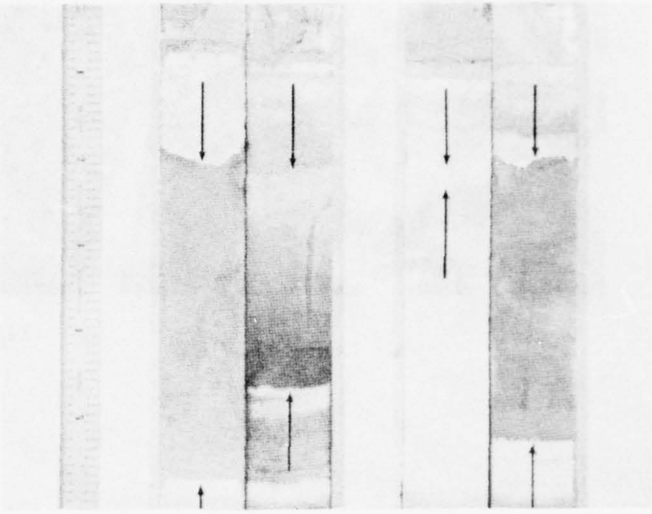
a. NORMAL VIEW 14,000X



b. PARALLEL VIEW 18,000X

FIGURE 40. SURFACE OF BARE 7075-T6 AFTER DEOXIDIZING

this surface to exhibit extremely poor durability, and nearly three inches of crack growth occurred in an adhesive manner. The fracture surface of a typical wedge test specimen for this surface character is shown in (1) of Figure 41. SEM inspection of a surface exhibiting characteristics similar to that shown in Figure 40 would result in the rejection of the panel.



(1) *DEOXIDIZED (COMPLETELY PRETREATED)*
(2) IMMERSED IN BATH FOR 20 MINUTES (NO VOLTAGE)
(3) TWO MINUTES INTERVAL BEFORE RINSE
(4) TEN MINUTES INTERVAL BEFORE RINSE

FIGURE 41. WEDGE TEST SPECIMENS FOR BARE 7075-T6

The surface character of the specimen of bare 7075-T6 which was immersed in the phosphoric acid bath for 20 minutes with no anodizing potential is shown in Figure 42. As with the deoxidized panel previously discussed, the character of the surface is quite different from that of the standard anodized surfaces. Note the presence of the film-like particulates on the surface of the specimen at the left of Figure 42a and near the top of Figure 42b. Preliminary analysis indicated that this film was copper depositing out of the anodizing bath. The bath had previously dissolved copper while anodizing other 7075-T6 panels. However, Auger analysis revealed excessive amounts of lead on this surface, indicating that this may be a lead deposit from the lead-lined anodizing tank. Figure 43 shows an Auger trace from the surface shown in Figure 42. The location of the primary lead peak is at 90 electron volts.

a. NORMAL VIEW 14,000X

b. PARALLEL VIEW 18,000X

FIGURE 42. SURFACE OF BARE 7075-T6 IMMERSED IN PHOSPHORIC ACID BATH FOR 20 MINUTES WITH NO VOLTAGE APPLIED

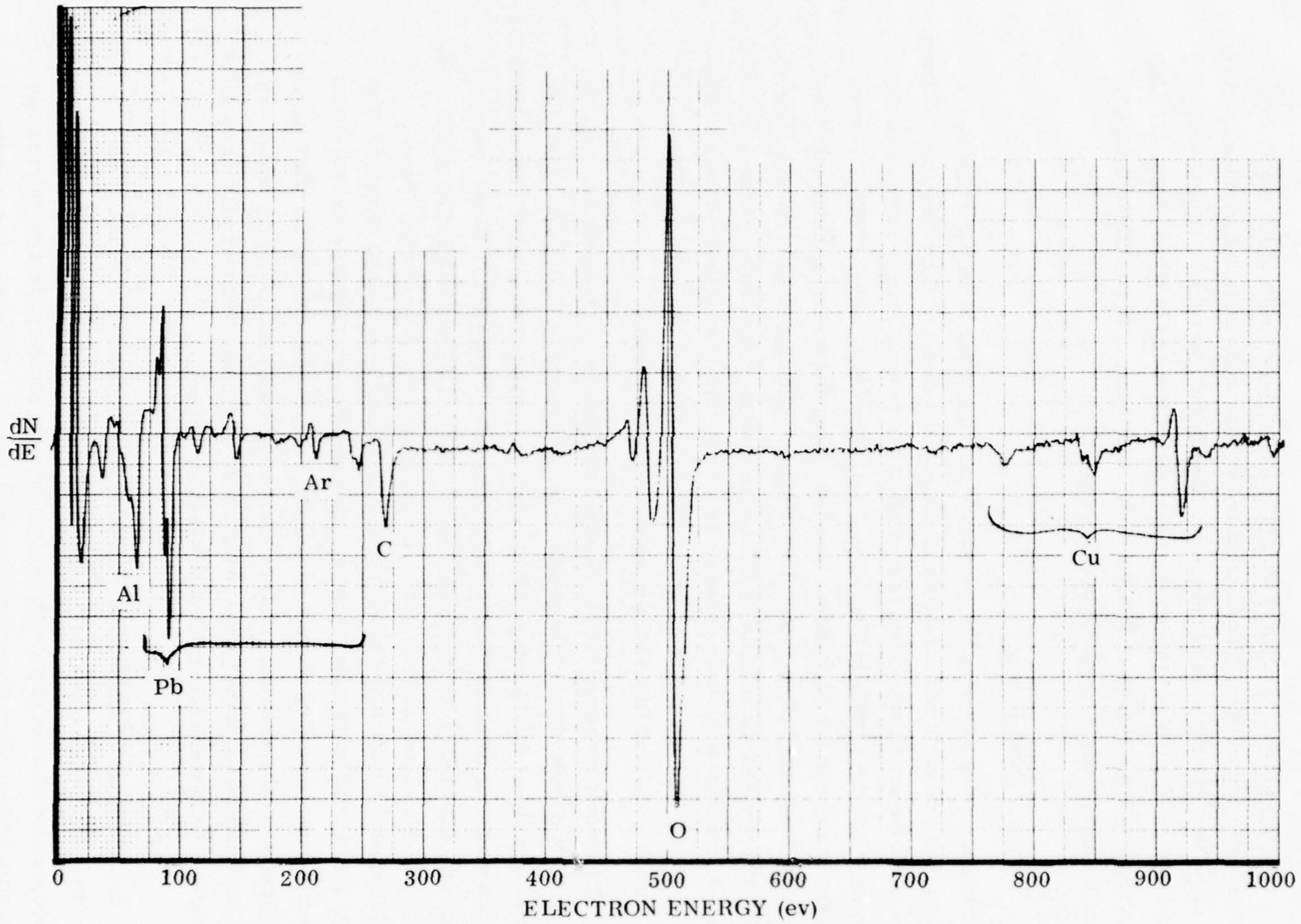


FIGURE 43. AUGER SPECTRUM OF BARE 7075-T6 SURFACE AFTER IMMERSION IN PHOSPHORIC ACID FOR 20 MINUTES WITH NO VOLTAGE APPLIED

The wedge test evaluation of the surface character shown in Figure 42 revealed extremely poor durability. The crack extended nearly three inches during exposure, and the failure was adhesive in character. The failed surface of a typical wedge test specimen corresponding to this surface character is shown in (2) of Figure 41. Any surface exhibiting a character similar to that in Figure 42 is rejectable from both a durability and from a microstructural standpoint.

10. Panel Rinsing

Panel rinsing following the phosphoric acid anodizing is an important factor affecting the character and durability of an anodized surface. The time interval from the moment the anodizing voltage is shut off to the moment rinsing begins was the variable selected for study in this phase. Four specimens of bare 7075-T6 were anodized at 10 volts for 20 minutes, then left suspended in the anodizing bath for 1, 2, 5, and 10 minutes before removal for rinsing. The character of the resulting anodic surfaces was documented by SEM examination. Thickness measurements of the anodic coatings revealed a decrease in coating thickness with increased holding times in the phosphoric acid bath before rinsing, as shown in Table 7. This is due to the acidic anodizing bath which dissolves the anodic layer.

SEM photomicrographs of the anodized surfaces left in the bath for 2 minutes showed little deterioration of the anodic coating, as seen in Figure 44. However, there is significant deterioration and attack of the anodic coating after 10 minutes in the anodizing bath, as shown in the photomicrographs in Figure 45. Extensive surface pitting was observed at low magnification (700X), and approximately 75% of the anodic coating was dissolved, as seen in the photomicrograph in Figure 45b. Panels exhibiting surface character similar to that in Figure 45 should be rejected. The wedge test durability results for the specimens having the 2-minute and 10-minute intervals prior to rinsing correlated with the SEM photomicrographs. That is, the 2-minute interval specimens exhibited acceptable wedge test behavior, whereas the 10-minute interval specimens had unacceptable wedge test behavior and nearly three inches of crack growth occurred in an adhesive manner.

E. PHASE V – STANDARD OPERATING PROCEDURE

The culmination of all of the knowledge developed throughout the program was the preparation of a set of procedures for using the scanning electron microscope for the quality control of anodized surfaces on aluminum. A specification was written outlining the procedure, equipment, and standards for inspection of anodized surfaces

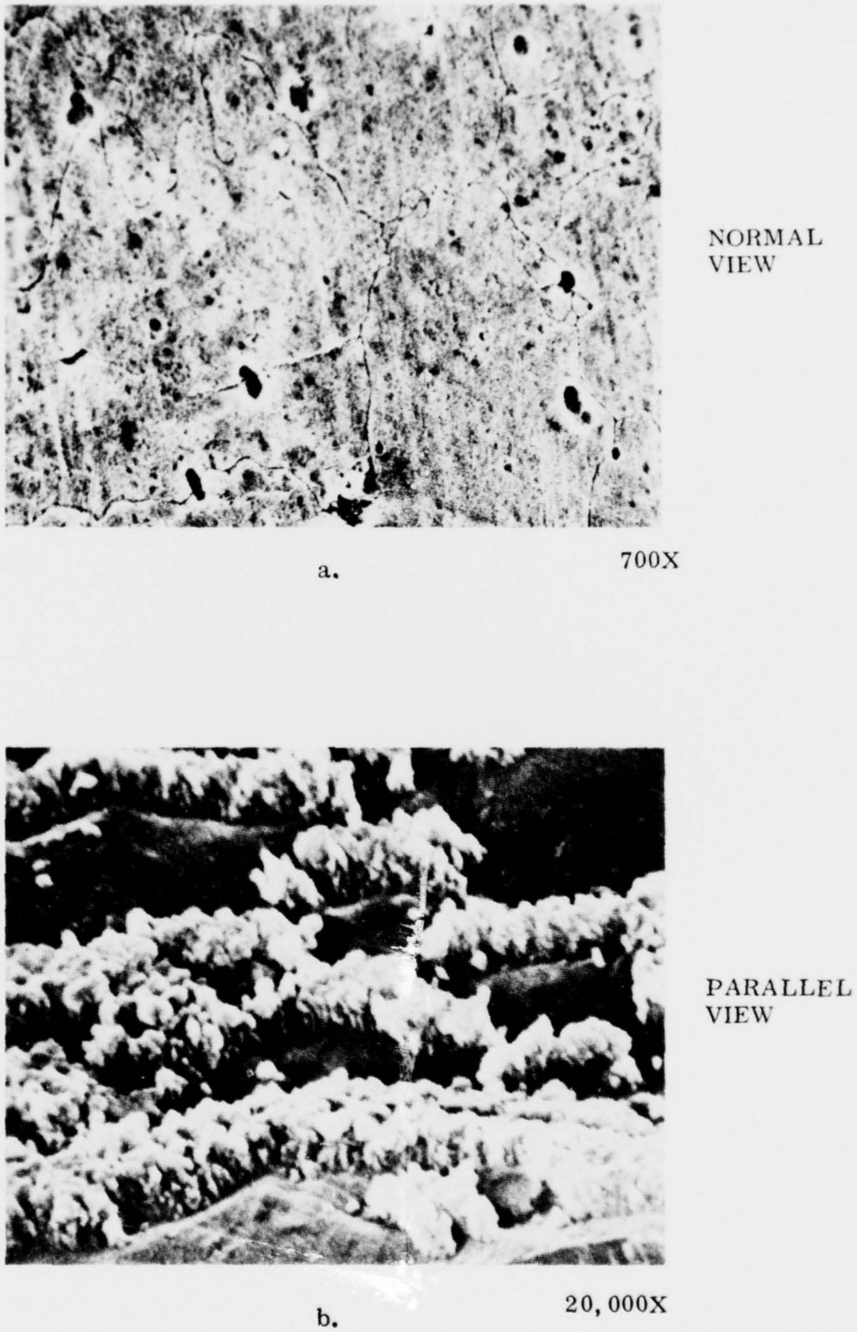


FIGURE 44. SURFACE CHARACTER OF BARE 7075-T6 — ANODIZED IN PHOSPHORIC ACID, THEN LEFT IN BATH 2 MINUTES WITH VOLTAGE OFF

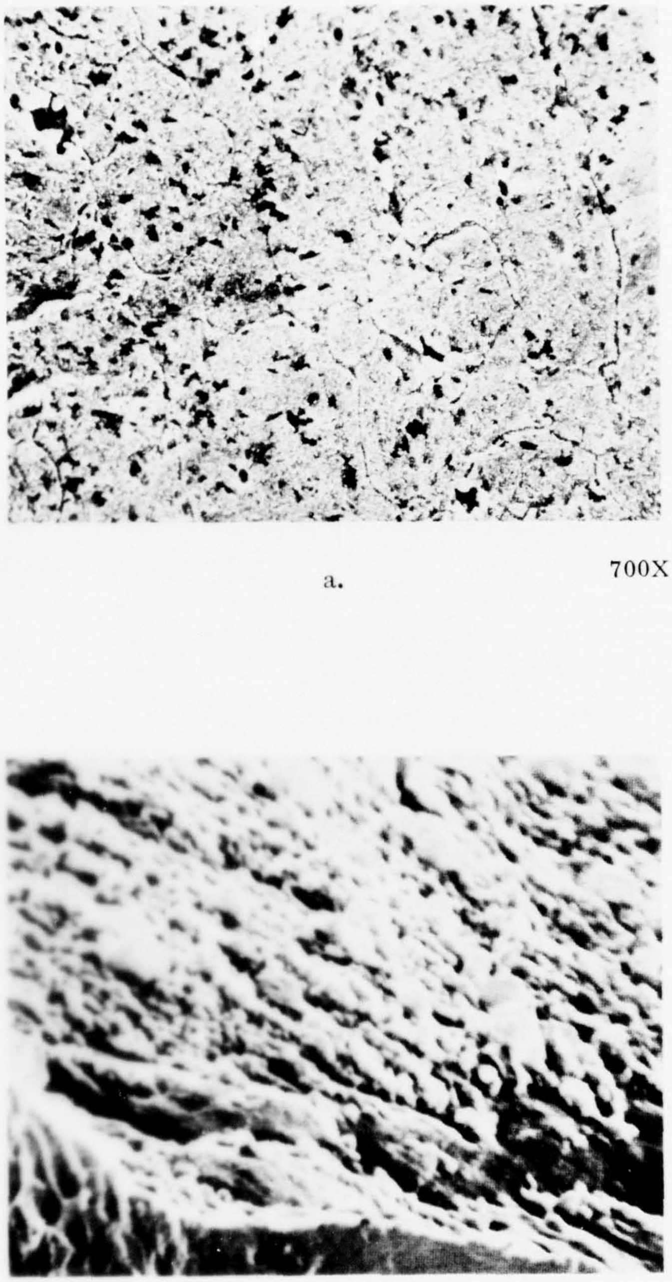


FIGURE 45. SURFACE CHARACTER OF BARE 7075-T6 — ANODIZED IN PHOSPHORIC ACID, THEN LEFT IN BATH 10 MINUTES WITH VOLTAGE OFF

based on the SEM characterization studies and the wedge test durability evaluation of the various permutations of phosphoric acid anodizing of bare 7075-T6. This specification is presented in its entirety in the Appendix.

Briefly, the procedures for inspection and quality control of phosphoric acid anodized panels of bare 7075-T6 are as follows:

1. Remove a tab specimen from the large anodized production panel. This specimen is considered representative of the production panel and rejection of the tab specimen will cause rejection of the entire production panel.
2. Prepare the tab specimen, of nominal dimension, 0.125-inch by 1-inch by 0.125-inch maximum thickness, for SEM examination by bending about 90° to crack the oxide and coat the specimen with about 200Å of gold.
3. Inspect the anodized surface of the tab specimen in the SEM. This includes the examination of the specimen at magnifications of 700X, 2800X, and 14,000X along a direction normal to the surface plane and the comparison of these results with the standard SEM photomicrographs shown in Figures A2, A3, and A5 in the Appendix. The criteria for acceptance of the panel include: sufficient grain boundary etching (700X, 2800X), uniformity of the oxide layer (700X, 2800X), absence of stains on the surface (700X), and adequate oxide cell development (14,000X). Failure to meet these acceptance criteria results in the rejection of the tab specimen and the production panel.
4. Determine the thickness of the anodic coating by SEM examination of its cross-section at a magnification of 20,000X. The thickness must be in the range of 3000Å to 5000Å, and should appear similar to the standard SEM photomicrograph shown in Figure A9 in the Appendix. Failure to do so results in rejection of the panel.

Despite the apparent sophistication of some of the equipment used in the inspection procedure, the time required for inspection and qualification of an anodized panel is minimal. Assuming that the specimens are prepared and inspected in groups of four (as they were during this program), it is estimated that the entire inspection procedure would take about 15-20 minutes per specimen, including about 6-8 minutes per specimen for cutting, bending, mounting, and gold coating, and about 9-12 minutes per specimen for SEM inspection and qualification.

It has been assumed in this inspection procedure that there is only one production panel in each anodizing run, and acceptance of the surface of the tab specimen constitutes acceptance of the production panel. However, if the production run consists of a multiple number of specimens, there is no guarantee that all of the panels have the same surface character. Therefore, some sampling procedure must be used with this inspection method.

III. CONCLUSIONS

1. This program demonstrated that the scanning electron microscope is a viable tool for characterizing anodic surfaces on aluminum alloys.

2. The anodic coatings resulting from phosphoric acid anodizing of bare 7075-T6 at standard conditions are reproducible in terms of physical, chemical, and crystallographic character.

3. The scanning electron microscope can be used to identify changes in anodic film character that have resulted from changes in anodizing procedures.

   a. The anodic coating growth rate for phosphoric acid anodizing of bare 7075-T6 is a parabolic function of time with about 90% of the oxide developing in the initial ten minutes of the 20-minute anodize.

   b. The anodic coating thickness for phosphoric acid anodizing of bare 7075-T6 varies linearly with anodizing voltage in the range of 0 to 20 volts with the standard voltage being 10 volts. The oxide cell size also increases with increasing anodizing potential.

   c. The anodic coating thickness is dependent upon the anodizing bath concentration range of 11 to 16 ounces per gallon as specified within the Boeing Specification. A lower bath concentration (12 compared to 14 ounces per gallon) yields a thinner anodic coating (3000Å compared to 4000Å).

   d. The time interval from the end of anodizing to the beginning of rinsing is critical to the retention of the anodic coating character. Given sufficient time the phosphoric acid bath dissolves both residual and anodic oxides. Immersion in the bath for 2-minutes prior to rinsing removes about 1000Å of the anodic coating.

4. There is a direct correlation between the surface character as seen with the SEM, and the durability of the bonded surface, as determined by wedge test evaluation.

a. The wedge test durability of bare 7075-T6 anodized in phosphoric acid was found to be dependent upon oxide thickness. Anodic coatings having a thickness greater than 3000Å exhibit acceptable wedge test behavior, whereas most coatings less than 2500Å exhibit unacceptable behavior.

b. The wedge test durability also exhibited a dependence upon the cell size of the anodic coating. In general, anodic coatings with a more highly developed oxide cell structure (larger cells) exhibited better durability than those coatings with less developed cell structure.

c. The wedge test durability of bare 7075-T6 anodized in phosphoric acid was insensitive to the pretreatment process used prior to anodizing. It was demonstrated that complete omission of the pretreatment process had no detrimental effect on the relative durability of the anodized surface. This result was unexpected, and requires additional investigation.

5. The scanning electron microscope is much more sensitive than the wedge test procedure in identifying changes in the anodic film character.

IV. RECOMMENDATIONS

1. Develop the same type of inspection procedure for other aluminum alloys and anodizing solutions.
2. The development of a better, more quantitative durability testing procedure, when coupled with surface characterization by the scanning electron microscopy, would lead to a better understanding of the interrelationship between the character of an anodized coating and the environmental durability of an adhesively bonded surface.

APPENDIX

SPECIFICATION FOR QUALITY CONTROL OF ANODIC COATINGS

1. SCOPE

1.1 This specification establishes the equipment, standards, and procedures for verification of the acceptability of anodic coatings following phosphoric acid anodizing of 7075-T6 aluminum alloy.

1.2 The acceptance criteria for the anodized surfaces of bare 7075-T6 are specified in 3.3.

2. APPLICABLE DOCUMENTS

2.1 The current issue of the following publication shall be considered part of this specification to the extent indicated herein.

2.1.1 BAC-5555, Boeing Process Specification: Phosphoric Acid Anodizing of Aluminum For Structural Bonding.

3. REQUIREMENTS

3.1 Equipment

3.1.1 The scanning electron microscope (SEM) shall consist of, but not be limited to, the following:

a. An electron source with accelerating potential of at least 15 KV.

b. Pre-aligned electro-magnetic lens system with coarse and fine objective lens controls for image focusing.

c. Enclosed vacuum column evacuated by an oil diffusion pump, and backed by a roughing pump. Pump-down time to a pressure of 1×10^{-4} torr after specimen insertion shall not exceed two minutes.

d. Double deflection scanning coils with two secondary electron scanning modes: one for visual observation and one for photographic recording.

e. Display screen (CRT) for viewing and photographic documentation.

f. Specimen stage capable of handling bent anodized specimens, with a minimum sample diameter of 0.75-inch and a minimum sample height of 0.50-inch, X- and Y-translation, and manual or electronic rotation and tilt from 0° to 90°.

g. Stepwise variable, direct reading magnification control from not greater than 100X to not less than 30,000X.

h. Electron-optical performance with a guaranteed resolution of at least 200A.

3.1.2 The equipment for preparation of the specimens prior to SEM inspection shall consist of the following:

a. A vacuum system capable of depositing a clean, uniform layer of gold 100 to 200Å in thickness, on the anodized surface. The coating process may include, but not be limited to, either vapor deposition or sputter-coating.

b. A mandrel, vise or other tool capable of holding the anodized aluminum specimens (nominally 0.125-inch by 1-inch by 0.125-inch maximum thickness) during bending in accordance with 3.2.1.b. The tool must be clean and must not induce contaminants such as oil or grease onto the anodized specimen.

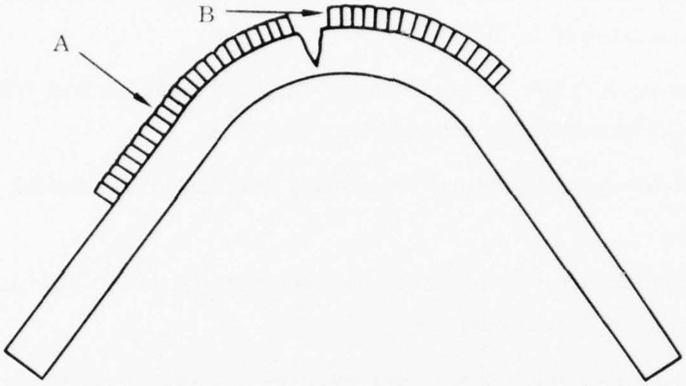
3.2 Process Requirements

3.2.1 Specimen Preparation Procedure Prior to SEM Inspection

a. Specimens shall be removed from anodized panels following phosphoric acid anodizing in accordance with Boeing Process Specification BAC-5555. The specimen size shall not exceed 0.125-inch by 1.0-inch by 0.125-inch in thickness, unless it is determined to be compatible with the size of the SEM specimen stage, as specified in 3.1.1.f. The specimens are to be representative of the anodic surface character of the larger panels.

Note: Specimen surfaces to be inspected shall be kept clean and free from all contaminants that may alter the character of the anodic coating. This includes, but is not limited to, grease, oils, vapors and fingerprints.

b. Manually bend the specimens slowly to produce a cracked anodic coating at the bend radius (see Figure A1).



A - Normal to Surface Plane - Inspect at 700X, 2800X, and 14,000X

B - Parallel to Surface Plane - Inspect at 20,000X

FIGURE A1. REPRESENTATION OF BENT ANODIZED SPECIMEN SHOWING DIRECTIONS OF SEM INSPECTION

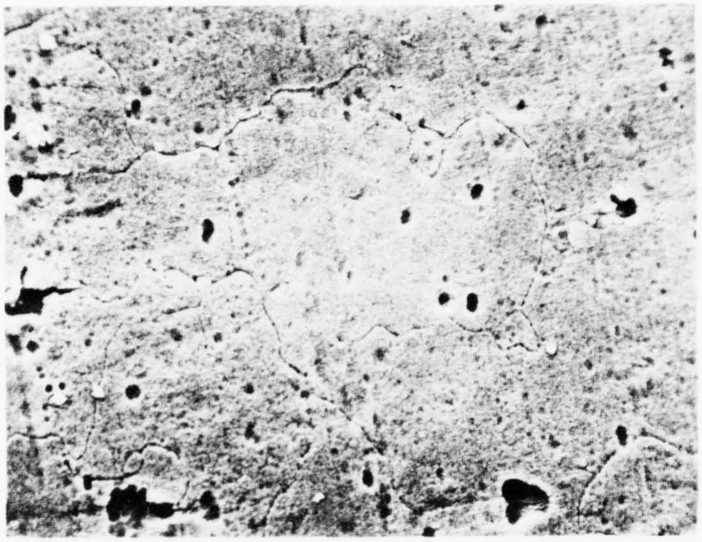
c. Mount the cracked specimen on a SEM mount (specimen stub) using a conductive paste, paint, or colloidal suspension. These may contain either silver or carbon as the conductive medium.

d. Apply a thin, uniform coating of high purity gold (about 100Å-200Å thick) on the mounted cracked specimen by vapor deposition or sputtering.

3.3 Acceptance Criteria

3.3.1 The acceptance criteria for phosphoric acid anodic coatings on bare 7075-T6 consist of a set of SEM photomicrographs showing the acceptable surface character as specified below:

a. The appearance of the phosphoric acid anodized surface of bare 7075-T6 when inspected along a direction normal to the surface plane (see Figure A1) at a magnification of 700X must appear similar to the surface shown in the SEM photomicrograph in Figure A2. Note should be made of the presence of the etched grain boundaries, which must be visible. Absence of grain boundary etching is not acceptable. Surface defects, such as holes and pits are acceptable.



NORMAL
VIEW

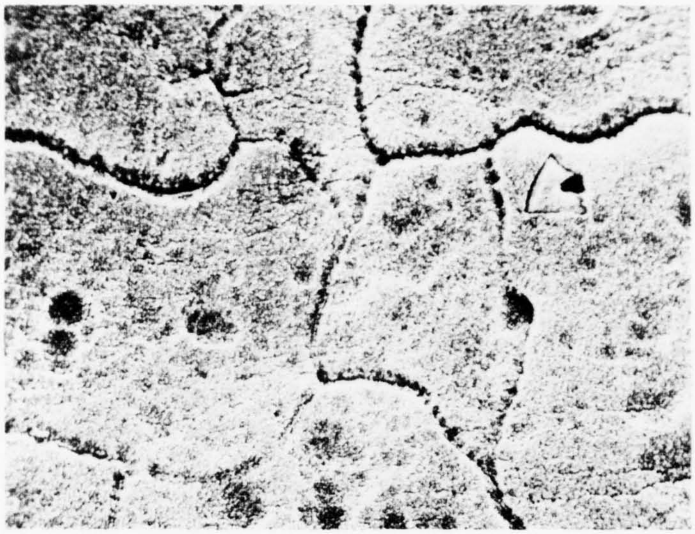
700X

FIGURE A2. GENERAL CHARACTER OF STANDARD SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

b. Inspection of the anodized surface at a magnification of 2800X must present an appearance similar to that shown in Figure A3. The grain boundary etching must again be evident and comparable in depth to that shown in A3. The absence of grain boundary etching as shown in the SEM photomicrograph in Figure A4, is not acceptable.

Note: Panels having some grain boundary etching, but to a lesser extent than in Figure A3, are acceptable. However, this condition is indicative of improper deoxidizing parameters.

c. Inspection at a magnification of 14,000X normal to the surface plane must reveal an anodic coating appearance similar to that shown in Figure A5. Verification of the presence of a porous anodic coating, by observation of the structure and porosity of the oxide layer, is critical to the acceptance of the anodized panel. Any surface not exhibiting a uniform, porous oxide structure between the grain boundaries is rejectable. Typical examples of rejectable surfaces are shown in Figure A6. In addition, the size of the oxide cells must be similar to those shown in the standard photomicrograph in Figure A5. The lower



NORMAL
VIEW

2800X

FIGURE A3. GRAIN BOUNDARY ETCHING OF STANDARD SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

limit of acceptability of the oxide cell size is shown in the SEM photomicrograph presented in Figure A7. Surface coatings having cell sizes between Figures A5 and A7 are acceptable. However, any surface exhibiting smaller oxide cells is rejectable, such as those surfaces shown in Figure A8. Surfaces such as these are indicative of improper anodizing procedures, such as insufficient anodizing time or voltage.

d. Inspection of the oxide thickness through its cross-section at a magnification of 18,000 to 20,000X shall reveal an image similar to that shown in Figure A9. Acceptance of the panel is based on the thickness of the coating measured from this image, which must be at least 3000Å, but not greater than 6000Å in thickness. Typical examples of oxide thickness on phosphoric acid anodized panels that do not meet this criteria and are rejectable are shown in Figure A10.

Note: A trend toward greater or lesser thicknesses is indicative of changes in the anodizing procedures; i.e., bath concentration, voltage, time, or poor electrical connections.

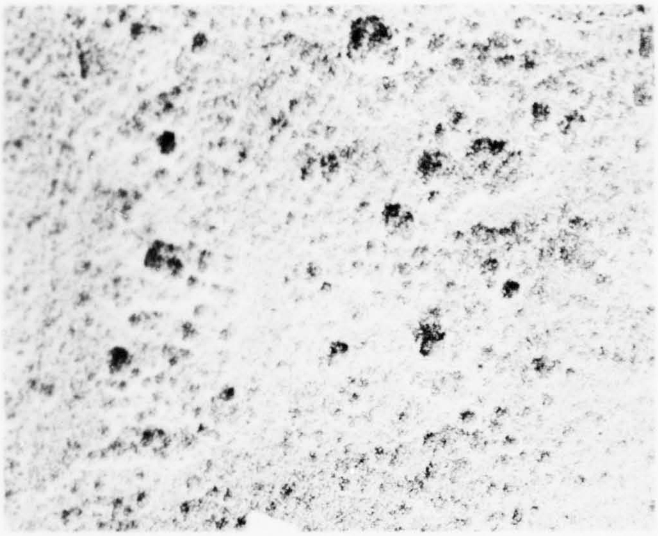


FIGURE A4. SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID AND REJECTABLE DUE TO IMPROPER DEOXIDIZING

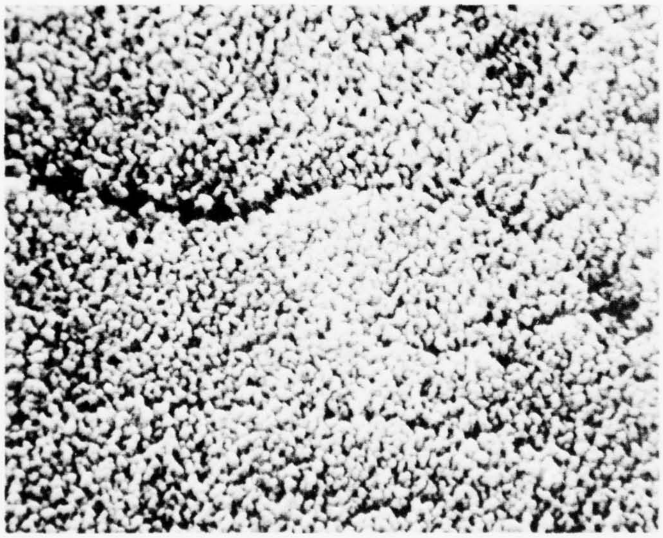
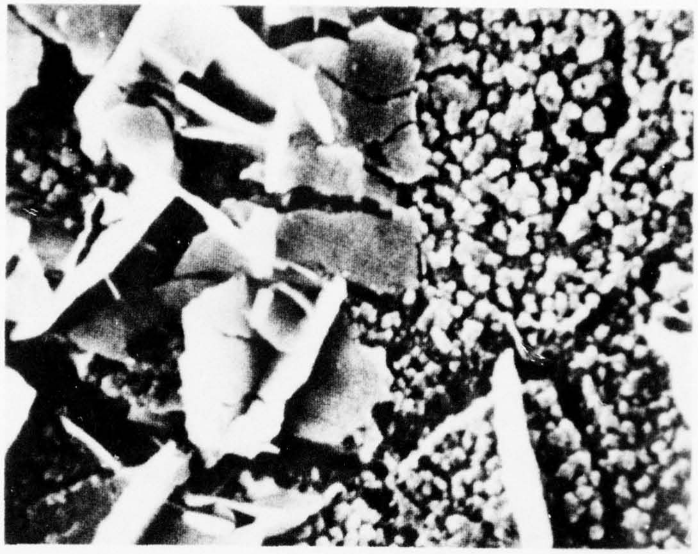


FIGURE A5. CELL STRUCTURE OF STANDARD SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID



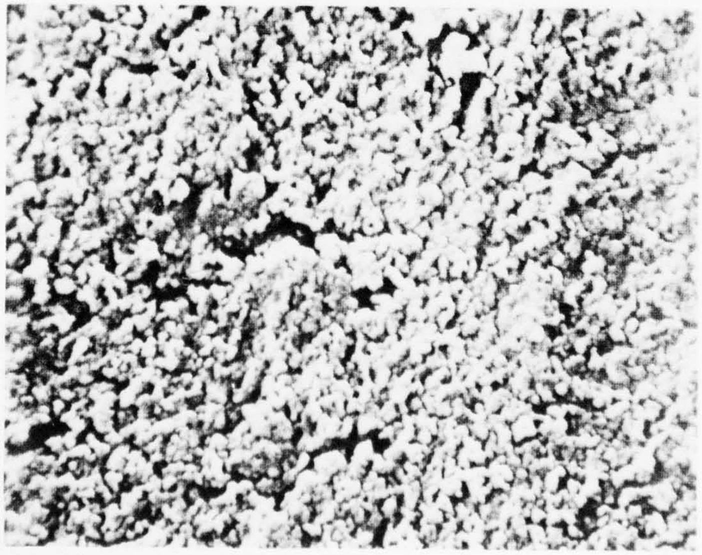


FIGURE A6. SURFACES OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID AND REJECTABLE DUE TO IMPROPER ANODIZING PROCEDURES

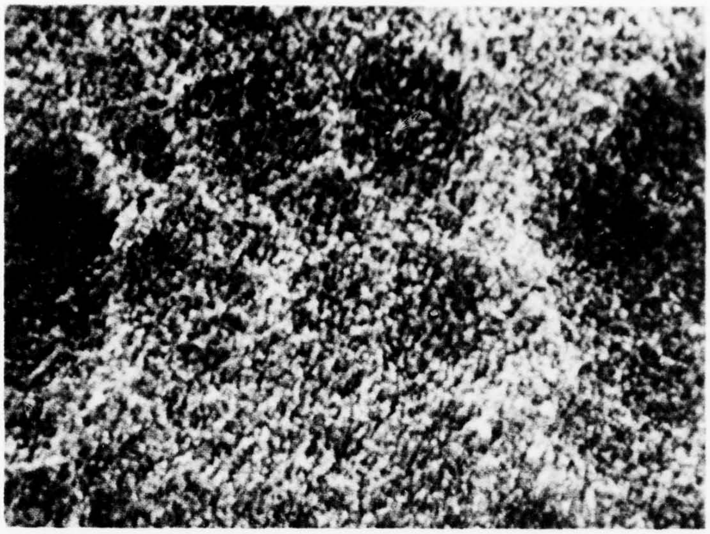


FIGURE A7. LOWER LIMIT OF ACCEPTABLE CELL STRUCTURE FOR PHOSPHORIC ACID ANODIZING OF BARE 7075-T6

3.3.2 SEM Inspection Procedure

a. Insert the gold-coated specimen (with stub) into the scanning electron microscope and execute the pump-down and start-up sequence. A vacuum pressure of 1×10^{-4} torr is required.

b. Inspect the anodic surface coating away from the bend radius as indicated by direction A in Figure A1. The coating shall be viewed at right angles (normal) to the surface plane and must pass the acceptance criteria at each of the following magnifications: 700X, 2800X, and 14,000X in accordance with 3.3.1.a-c.

c. Determine the thickness of the anodized coating by inspection parallel to the surface, at a magnification of 20,000X, as indicated by direction B in Figure A1. The thickness must be within the limits specified in 3.3.1.d.

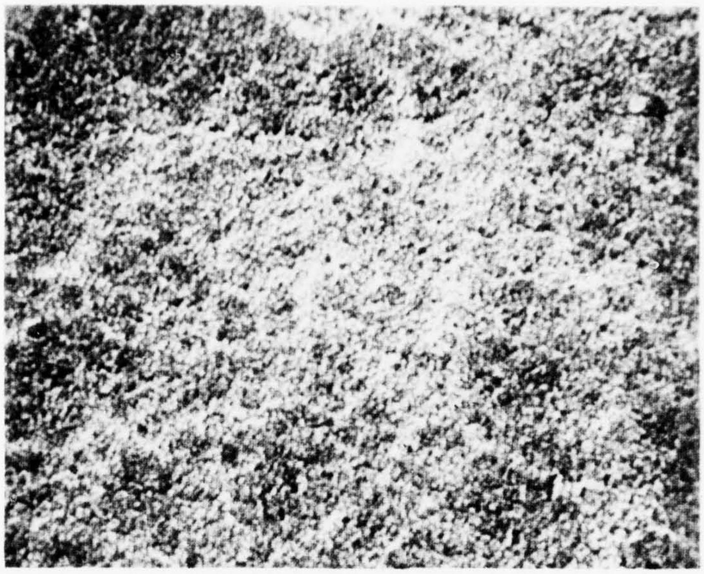


FIGURE A8. SURFACES OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID AND REJECTABLE DUE TO INADEQUATE OXIDE CELL STRUCTURE

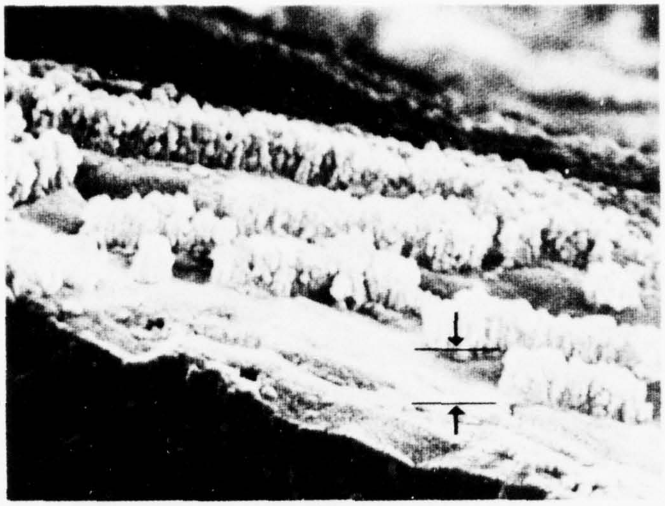


FIGURE A9. OXIDE THICKNESS ON STANDARD SURFACE OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID

3.4 Facility Requirements

3.4.1 Locate equipment, specimens, and records in a clean, well-lighted area free of noise and vibration and sufficiently removed from the production facilities to preclude contamination by substances detrimental to both specimens and equipment. This includes, but is not limited to, dusts, acids, oils, greases, solvents, fumes, and vapors.

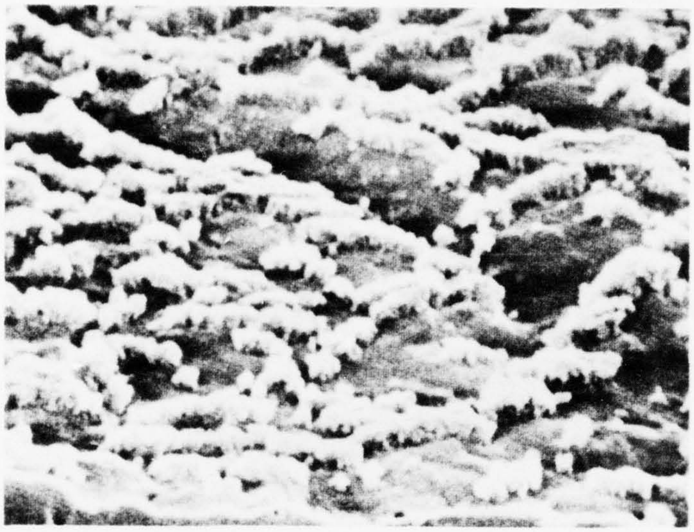
3.4.2 Optimum performance of the scanning electron microscope is achieved by locating the equipment in an area that can be darkened.

3.5 Qualification of Personnel

3.5.1 All personnel operating the inspection equipment and accepting or rejecting anodized panels shall be certified by:

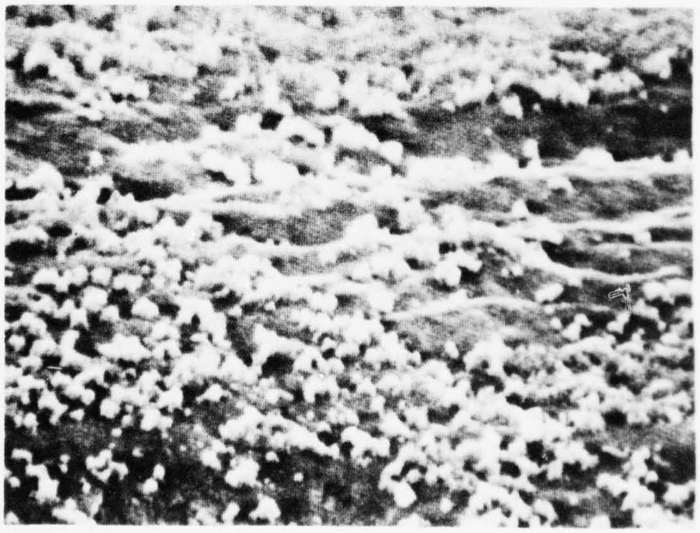
a. Completion of a training course on the operation of the sample preparation and inspection equipment.

b. On-the-job training by a certified operator.



PARALLEL
VIEW

17,000X



PARALLEL
VIEW

18,000X

FIGURE A10. SURFACES OF BARE 7075-T6 ANODIZED IN PHOSPHORIC ACID AND REJECTABLE DUE TO INADEQUATE COATING THICKNESS

4. QUALITY ASSURANCE

4.1 Manufacturing and Inspection Control

4.1.1 Maintain an inspection procedure that will allow traceability of tab specimen back to the larger anodized panel.

4.1.2 Inspection records shall be kept complete and available on the anodic coating thicknesses of each panel inspected, as well as any comments by the inspector on any abnormalities or deviations from normal that develop in the character of the anodic coating.

4.2 Equipment and Standards

4.2.1 All equipment shall be maintained in working order in accordance with 3.1.

4.2.2 Periodic servicing of the scanning electron microscope shall be required to maintain a minimum working resolution of 200Å.

4.2.3 A reference file shall be maintained of current SEM photographs of representative acceptabie and rejectable anodic surfaces.

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3. Douglas Aircraft Company, McDonnell Douglas Corporation, PABST ALERT Technical Bulletin, March 1976, F33615-75-C-3016.

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