

AO-A083 202

AIR FORCE MATERIALS LAB WRIGHT-PATTERSON AFB OH F/G 11/6
THIN ANODIC OXIDE FILMS ON ALUMINUM ALLOYS AND THEIR ROLE IN TH--ETC(U)
FEB 80 N T MCDEVITT, J S SOLOMON
AFML-TR-79-4216

UNCLASSIFIED

NL

1-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

5-1

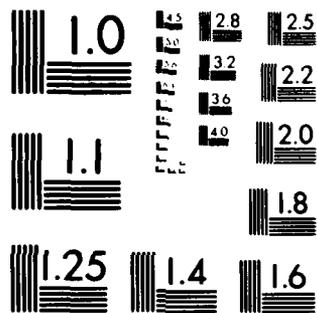
END

DATE

FORMED

5 80

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AFML-TR-79-4216

(2) LEVEL II
B.S.

ADA 083202

**THIN ANODIC OXIDE FILMS ON ALUMINUM ALLOYS
AND THEIR ROLE IN THE DURABILITY
OF ADHESIVE BONDS**

NEIL T. MCDEVITT

*MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION*

J. S. SOLOMON

*UNIVERSITY OF DAYTON RESEARCH INSTITUTE
DAYTON, OHIO 45469*

FEBRUARY 1980

TECHNICAL REPORT AFML-TR-79-4216
Final Report for period January 1979 to August 1979

DTIC
ELECTE
S D
APR 21 1980
B

Approved for public release; distribution unlimited.

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

80 4 17 129

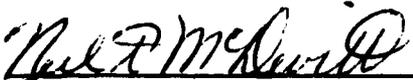
FILE COPY

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

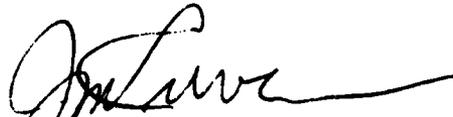


NEIL T. MCDEVITT
Mechanics & Surface Interactions Br.
Nonmetallic Materials Division



S. W. TSAI, Chief
Mechanics & Surface
Interactions Br.
Nonmetallic Materials Division

FOR THE COMMANDER



J. M. KELBLE, Chief
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/MLBM W-PAFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

9 Final rept. Jan-Aug 79

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

14

6

10

Janes

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-79-4216	2. GOVT ACCESSION NO. AD-A083202	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Thin Anodic Oxide Films on Aluminum Alloys and Their Role in the Durability of Adhesive Bonds		5. TYPE OF REPORT & PERIOD COVERED Final Jan. 1979-Aug 1979
7. AUTHOR(s) Neil T. McDevitt AF Materials Laboratory P.S. Solomon, University of Dayton Research Institute, Dayton, Ohio 45469		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Materials Laboratory (AFML/MBM) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, Ohio 45433		8. CONTRACT OR GRANT NUMBER(s) Inhouse Report
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory (AFML/MBM) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62102F, Project 2419/Task 02, Work Unit 04, WUD 44
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Same as above		12. REPORT DATE 11 FEBRUARY 1980
		13. NUMBER OF PAGES 24
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aluminum alloys Anodization Phosphoric acid Aluminum		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The structure and chemical composition of anodic oxide films on aluminum alloys is discussed with reference to pure aluminum. The potential effects of these inhomogeneities are also discussed with reference to the durability of adhesively bonded structures.		

11 2419
17 02

15 29

012520

JAC

FOREWORD

This technical report was prepared by Neil McDevitt, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio, and Mr. James S. Solomon, University of Dayton Research Institute, Dayton, Ohio. The work was initiated under Project 2419 "Nonmetallic and Composite Materials", and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

This report covers work conducted inhouse during the period January 1979 through October 1979. The report was released by the author in October 1979.

The authors are especially grateful to Mr. William Baun for his technical assistance and valuable advice.

S DTIC
ELECTE **D**
APR 21 1980
B

ACCESSION for		
NTIS	White Section	<input checked="" type="checkbox"/>
DDC	Buff Section	<input type="checkbox"/>
UNANNOUNCED		<input type="checkbox"/>
JUSTIFICATION _____		
BY _____		
DISTRIBUTION/AVAILABILITY CODES		
Dist.	AVAIL. and/or	SPECIAL
A		-

TABLE OF CONTENTS

SECTION		PAGE
I	BACKGROUND	1
II	INTRODUCTION	3
III	LITERATURE REVIEW OF ANODIZED ALUMINUM	5
	1. ANODIZATION	5
	2. STRUCTURAL CHARACTERISTICS	6
IV	DISCUSSION OF ANODIC FILMS ON ALUMINUM ALLOYS	10
	1. ANODIZATION AND STRUCTURAL CHARACTERISTICS	10
	2. ANODIC OXIDE FILM COMPOSITION	14
	3. POTENTIAL EFFECTS OF MICROCONSTITUENTS IN THE ANODIC OXIDE LAYER	16
V	CONCLUSIONS	19
	REFERENCES	20

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Thermogram of Boehmite, Bayerite, and Anodic Oxide on Aluminum.	7
2	Porous Oxide and Barrier Layer on Aluminum.	9
3	Anodic Oxides on Aluminum and 2024 Aluminum.	13

LIST OF TABLES

TABLE		PAGE
I	Nominal Chemical Composition of Aluminum Alloys	11

SECTION I
BACKGROUND

The full utilization of aluminum alloys in metal-to-metal adhesively bonded structures requires a thorough knowledge of all the factors that go into the fabrication of a bonded joint. The major factors that must be considered in the study of adhesive bonding technology are:

A. Components of the adhesive joint

- 1) metallurgy of the adherend
- 2) surface chemistry of the adherend
- 3) prepared oxide layer
- 4) primer chemistry
- 5) adhesive system chemistry
- 6) cure cycle chemistry
- 7) synergism of each created interface

B. Dynamic environment

- 1) stress
- 2) humidity and other atmospheric gases
- 3) temperature

C. Failure analysis

- 1) fracture
- 2) fatigue
- 3) corrosion

Studies involving the appropriate permutations and combinations of A, B, and C are needed to generate a data base for advancing our knowledge in the area of life expectancy of adhesively bonded primary structures. Therefore, the solution to the problem of life prediction will not be found in the study of just one of the above factors. However, it is important to avoid misunderstanding the significance of the above discussion. Studies must be accomplished for each individual factor in the bonded joint, but it should be understood that the results from an individual factor study must be combined with other studies in order to obtain accurate answers for the total system. Only after an

accumulation of sufficient experience in correlating test data from each individual factor study can any degree of confidence be justified in predicting the life expectancy of a bonded structure.

SECTION II INTRODUCTION

The purpose of this report is to bring into perspective one of the component parts of an adhesive joint, the prepared oxide layer as formed on aluminum alloys. The formation and properties of oxide films formed on pure aluminum have been reviewed extensively in the literature (References 1-4) by a number of authors; however, the alloys of aluminum have not received the same in-depth study (References 5,6).

The prepared oxide layer used as a surface preparation for bonded joints has always been considered one of the major links in the total system. The durability of the joint is greatly dependent on the integrity of the oxide to the metal, and oxide to the adhesive. The oxide layer must be thin enough to transfer the load to the metal adherend, but thick enough to provide some protection for the alloy from the environment.

From 1950 through 1965 the only surface preparation for adhesively bonded aluminum aircraft structures was a chemical treatment called the FPL etch (Reference 7). This treatment provided a more durable surface with reference to the other solutions used at that time. However, it still was not really stable and was sensitive to service in seacoast environments (Reference 8). Data from failed bonded structures that had seen actual service conditions (Reference 9) indicated a study of pre-bond surface preparations was necessary. The work of Smith (Reference 10) in the early 1970's highlighted the electrochemical vagaries of the FPL etch method. The floating potential of this chemical etch bath had to be maintained by specific amounts of added copper ions in order to achieve the desirable oxide layer for bonding.

During this same period, it became very apparent to scientists and engineers that the surface plays a most important role in the interaction of materials. The first attempt at the characterization of adherend surfaces was made by Wegman (Reference 11). Over

the next several years techniques and instrumentation for studying surfaces became prominent (References 12-14). These surface chemistry studies helped to obtain a better understanding of the oxide layer generated by various chemical preparations used on aluminum.

Anodization is another method of generating an oxide layer on a metal surface. The process of anodization produces a coating of metal oxide or hydroxide on a metal anode by the electrochemical oxidation (applied potential) of that anode in contact with an electrolyte. Anodization has been utilized in metal-to-metal adhesive bonding since the early 1960's. At that time sulfuric and chromic acid were the primary electrolytes (References 15, 16). Forming an oxide layer with these electrolytes never became a prominent method of surface preparation for adhesive bonding in the United States. Chromic acid has been used in Europe for adhesive bonding over the past fifteen years with no particular published problems (Reference 17). In the early 1970's Boeing Aircraft Company* looked at the anodization procedure and developed a process using phosphoric acid as the electrolyte.

This report reviews the literature on anodic oxide films formed on pure aluminum and discusses these results with reference to work from our laboratory and published data on anodic oxide films formed on aluminum alloys.

*Boeing Aircraft Company Process Specification BAC 5555

SECTION III
LITERATURE REVIEW OF ANODIZED ALUMINUM

1. ANODIZATION

Anodization, simply stated, is the flow of electric current between two electrodes. The electrodes are separated by an electrolyte which is a conductor, and with the passage of current a metal oxide layer will form on the positive electrode (anode). This reaction occurs most readily when the anode is aluminum. A major portion of the data presented in the literature has been concerned with theory and the formation of oxide films on high purity aluminum (References 1, 3). Water is the main solvent used in the electrolytic bath; however, there have been some studies (References 18, 19) using organic solvents and fused salts. The formation and structure of an anodic oxide layer on an anode may be controlled by the interplay of the following anodization conditions:

- A. Electrolyte
 - 1) type
 - 2) concentration
 - 3) purity
- B. Parameters
 - 1) voltage or current
 - 2) time
 - 3) temperature
- C. Anode and Cathode (Reference 46)
 - 1) material used
 - 2) ratio of areas

The application of direct current to the anode is the normal anodization process, although alternating current is used in certain procedures. The direct current application generally employs two methods; 1) applying a fixed voltage to the anode and monitoring the current or; 2) holding the current constant while monitoring the voltage of the system.

An excellent review of the oxides and hydroxides formed on aluminum has been published by Wefers (Reference 20). Wefers' paper is concerned mainly with crystalline oxide compounds, although gelatinous alumina is discussed. An early paper by Harrington and Nelson (Reference 21) reported that the composition of anodic oxide films formed on aluminum in different electrolytes are mostly amorphous compounds of random structure. Anodic oxide films are also compared to the aluminum-water reaction (References 22, 23). The two compounds usually obtained from this reaction are boehmite and bayerite. The data shown in the thermogram in Figure 1 does not show any direct relationship of anodic aluminum oxide to either compound.

Since the formed anodic oxide is amorphous the proof of its identity has fallen heavily on molecular spectroscopy, in particular, infrared. Infrared data (Reference 22) show the oxide layer to be primarily composed of a "pseudo" boehmite structure which contains both electrolyte anions and water. Thus, the formed oxide has to be considered a complex function of its forming parameters.

2. STRUCTURAL CHARACTERISTICS

A continuous film usually is formed on pure aluminum under an applied potential. Depending on the solubility of the formed anodic oxide in the particular electrolyte employed, two separate oxide structures may be obtained. In electrolytic systems where the solubility is low, the formed oxide will have a resistance of thousands of ohms. Under these conditions, the current will become less as the oxide layer becomes thicker and eventually it will stop growing when the driving force of the electrochemical reaction is turned off. The oxides formed in this manner are called barrier layers and their thickness is directly proportional to the applied potential. The refractive index of the barrier layer has been studied (Reference 31) and reported to be 1.64. The term barrier layer implies an oxide film of different character than the cell walls. In the opinion of the authors the barrier

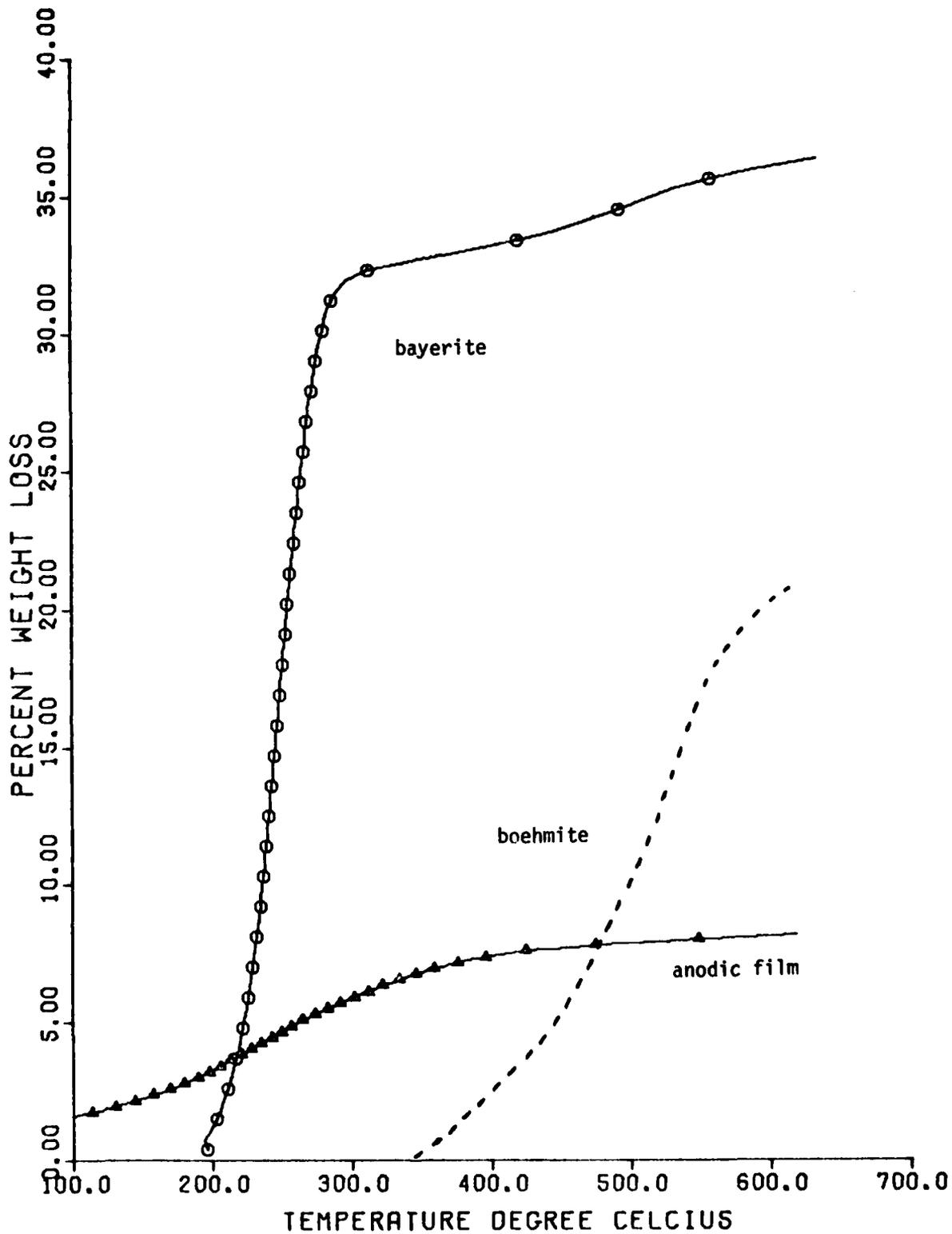


Figure 1. Thermogram of Boehmite, Bayerite, and Anodic Oxide on Aluminum.

layer is composed of the same structure and density as the cell walls, with the exception of some incorporation of the acid anion. If the oxide is somewhat soluble in the electrolyte then the thickness of the oxide film will be influenced by this dissolution parameter. In this type of electrolytic system the bath continues to draw current with the growth limiting factor proportional to the equilibrium value established between formation and dissolution of the oxide film. These anodic oxide films are characterized by their porous structure. The two types of films are shown in Figure 2. One of the main characteristics of the porous oxide structure that all investigators seem to agree upon is the development of the barrier layer at the base of the porous structure (Reference 24).



POROUS TYPE STRUCTURE



BARRIER TYPE STRUCTURE

Figure 2. Porous Oxide and Barrier Layer on Aluminum.

SECTION IV
DISCUSSION OF ANODIC FILMS ON ALUMINUM ALLOYS

If the formation of an anodic oxide layer on pure aluminum seems complex it understandably becomes more complex with aluminum alloys. When elements are added for alloying purposes, they can appear in the alloy in several different forms; 1) may be in solid solution, 2) as microparticles of the elements themselves or, 3) be present as intermetallic compounds formed in combination with aluminum. When these microconstituents become part of the surface they will not respond uniformly to the various chemical or electrochemical treatments.

The effects of chemical treatments on the surface composition of a number of aluminum alloys have been reported (References 25, 26). Table I shows the bulk chemical composition of the alloys studied. These studies indicate that the 2024 alloy series can have magnesium and copper on the surface after various treatments. Copper may also be present on the 7075 alloy surface following chemical treatments. Zinc is not normally found at the surface of this alloy. Traces of the elements associated with various chemical treatment solutions can be detected on the surface of the treated alloy. These studies indicate the importance of a chemical analysis of the surface of each alloy after every treatment.

Various thermal treatments may also be responsible for moving some of the alloying constituents to the surface (References 27, 28).

1. ANODIZATION AND STRUCTURAL CHARACTERISTICS

When a specimen of aluminum is made the anode in a common acid electrolyte, the formed anodic oxide is uniformly distributed across the surface. The conversion of aluminum ions to oxide is quite efficient and there is no evolution of gas at the anode.

The anode does not react as efficiently when the material is an aluminum alloy. Gas evolution at the anode is prominent

TABLE I
NOMINAL CHEMICAL COMPOSITION OF ALUMINUM ALLOYS

Alloy	Si	Cu	Mn	Mg	Cr	Zn	Zr
2024	---	4.5	0.6	1.5	---	---	---
7050	---	2.3	---	2.25	---	6.2	0.12
7075	---	1.6	---	2.5	0.3	5.6	---
6061	0.6	0.25	---	1.0	0.2	---	---

particularly when it is a copper containing alloy (Reference 29). Therefore, the various aluminum alloys will behave differently electrochemically since they will have microconstituents in the surface that give different metallurgical structures. Evidence of the relation between surface composition and electrochemical reactivity has been determined in a study of the formed oxide thickness on the various alloys under similar anodizing conditions (Reference 30). With reference to pure aluminum, all of the alloys have a thinner oxide layer for an anodization time of twenty minutes. The alloys having the highest copper content will have the thinnest oxide layer. This means a higher voltage would be required for these alloys in order to achieve the same oxide thickness as generated on pure aluminum. Therefore, different alloys should not be anodized at the same time in the same bath because the alloy with the higher anodization efficiency will draw more current (areas being equal) and grow a thicker oxide layer.

The formation of porous anodic layers was discussed with reference to pure aluminum anodes. The oxide film formed on an aluminum alloy anode in phosphoric acid does not generate the same classic structure as exhibited for pure aluminum. An example of the different structures can be observed in Figure 3. Both structures were formed in an 0.1M phosphoric acid bath at 60 volts for 60 minutes. The oxide layer on the alloy is porous but does not give the same classic picture as the pure aluminum anode. It would be more accurate to call the aluminum oxide layer "columnar" since the term porous is nondefinitive. The barrier oxide layer normally observed at the base of the columnar structure on pure aluminum is not apparent in the micrograph of the alloy oxide. We have not been able to observe a continuous barrier layer on any of the alloys studied by scanning electron microscopy. The work of Zahavi (Reference 32) may offer a partial explanation why a continuous barrier layer is difficult to obtain. This particular work was concerned with alloys containing dispersed Al_3Fe phases; however, it should be applicable

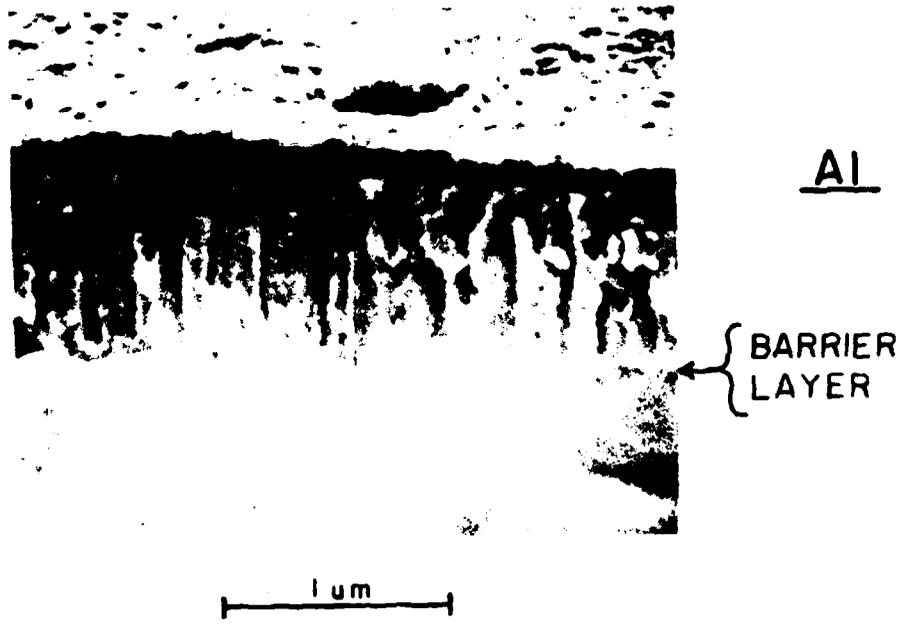


Figure 3. Anodic Oxides on Aluminum and 2024 Aluminum.

to Al-Cu microconstituents in the alloys studied in this report. They observed the microconstituent particles were removed on anodization and the re-anodization of the formed pit was frequently less regular than for the cases where no particles were involved. At the same time, if these particles were not completely removed on anodization, they would block continuous oxide growth along the oxide-metal interface giving a noncontinuous film at this surface.

2. ANODIC OXIDE LAYER COMPOSITION

The lack of a classic columnar structure and barrier layer on the aluminum alloys studied can be attributed to the electrical nonuniformity of the surface. Some of the microconstituents that may contribute to this nonuniformity are; CuAl_2 , MgZn_2 , Al-Mg, Al-Cu-Mg, and Al-Cu-Fe. The anodization characteristics of these materials have been studied with sulfuric acid as the electrolyte (Reference 5). We presume the reaction of these materials with phosphoric acid would be somewhat more aggressive. Under specific anodizing conditions, these materials may dissolve, anodize, or remain unchanged in the oxide layer. Anodization, if it occurs, most likely will be at a rate entirely different than for the aluminum phase. Each oxide structure and composition will be dependent on the alloy, pre-anodized surface, electrolyte, concentration, applied voltage, temperature, and time in bath.

It has been shown (Reference 33) that chemical elements present in the pre-anodized layer can find their way to the final anodic oxide surface layer. The porous anodic oxide can easily have distributed throughout its thickness all of the elements present on the pre-anodized surface. Where these elements come to rest in the oxide layer is dependent on their mobility rate under an applied potential.

Mackintosh, Brown, and Plattner (Reference 34) studied the mobility of metallic foreign atoms during the anodic oxidation of aluminum. They observed, for example, that copper remained

at the metal-oxide interface when implanted in the metal surface and then anodized with ammonium pentaborate. Using phosphoric acid (1.0M) as an electrolyte, Solomon (Reference 30) observed a narrow band of copper at the metal-oxide interface after one minute of anodization; however, after 10 minutes the copper band became more diffuse. Strehblow (Reference 35) examined anodic oxide films from aluminum/copper alloys by Rutherford backscattering and also observed copper accumulating at the oxide-metal interface. Fluoride ions present on the surface before anodization will pass into the oxide layer, as pointed out by McDevitt and Baun (Reference 33).

Calcium, strontium, and barium have been shown (Reference 35) to move outwards under an applied potential. Magnesium should react in this same manner because of its relationship to this family of elements. Solomon (Reference 30) noted that sputter profiles through oxides grown on 2024 aluminum did not show the presence of magnesium. Magnesium, however, can be found at the oxide-metal interface after various treatments, indicating this element can be mobile under anodic conditions.

Anion incorporation into the oxide layer is directly related to the acid bath used for anodization. Data from an X-ray fluorescence study (Reference 36) shows phosphorus to be present in an oxide layer formed on a pure aluminum anode in a phosphoric acid bath. The concentration of phosphorous (as the anion) is shown to be directly related to the final voltage when formed under constant current conditions. Solomon (Reference 30) reports the same findings on pure aluminum anodes utilizing Auger profiles. However, an analogous study performed on 2024 aluminum shows the phosphorus incorporation into the oxide layer to be practically constant for all voltages. Unlike the pure aluminum oxide layer, the oxide layer formed on the alloy shows phosphorus concentrated in the outermost 30% of the film.

3. POTENTIAL EFFECTS OF MICROCONSTITUENTS IN THE OXIDE LAYER

When investigating the surface energy, electrochemical, and mechanical properties of the formed oxide layer, it is necessary to consider all of the microconstituent particles at the oxide-metal interface, and in the mass of the oxide layer. These particles form a complex structure and the interaction of this structure with the environment determines the durability and corrosion properties of the oxide layer.

Corrosion of an alloy is associated with the flow of electric current between various local anodic and local cathodic regions on the surface. Providing a conducting environment is present, these regions will be associated with the microconstituents in the oxide layer and at the oxide-metal interface. The rate of any electrochemical corrosion reaction will depend on the microconstituents location to each other, quantity, size, and relative potential of these regions.

Most corrosion studies reported in the literature for alloys usually are concerned with simple binary alloy systems (References 37, 38). The complex oxide structure associated with the multi-component alloys will only allow the binary studies to be used as baseline references. The overall critical effect of corrosion will be directly related to the application of the aluminum alloy as a structural material. In the case of adhesively bonded structures, the integrity of the bondline is of prime importance; therefore, durability of the structure will require a reduction or elimination of corrosion in this critical area.

The more inhomogeneous the surface the more susceptible it will be to general corrosion. As a general rule of thumb, the area ratio of the local cathode to the local anode should be approximately 0.1 (References 39, 40). This is one reason why clad aluminum alloys are not suitable as adherends in bonded joints because the area ratio $CATH/AN = 1$. The rate of corrosion at the local cell sites will also depend on the potential difference between the cells.

Magnesium has proven to be detrimental to the oxide-metal interface (Reference 41). Magnesium is anodic to aluminum so it will corrode and when located in the bondline it will reduce the durability of the structure. Magnesium can form a number of intermetallic compounds, Mg_2Al_3 , $MgZn_2$, and $CuMgAl_2$ that are anodic to both aluminum and $CuAl_2$. A bondline containing these microconstituents will fail quickly under humidity and stress.

Copper will also be present (as intermetallic compounds) on the surface of 2024 and 7075 aluminum that has been anodized in a phosphoric acid electrolyte. The sign of the electrode potential (assuming $Al = 0$) will change in the case of copper with reference to magnesium. Copper will be more positive and become the cathode in the system. This form of corrosion will lead to pitting of the bulk aluminum. The mechanism of the initiation of pitting corrosion of aluminum alloys is still somewhat cloudy (Reference 42). We know copper is present on the pre-anodized surface and an undetermined amount will remain at the oxide-metal interface after 10 minutes of anodizing in phosphoric acid. Quantifying the amount of copper at this interface is very difficult; however, studies in our laboratory (Reference 43) have shown 2024 and 7075 to pit badly in an aggressive salt environment, and analysis of these pits shows copper to be present in all cases. The ratio of the area of the copper cathode to the aluminum anode will be small so the rate of pitting should be slow unless amplified by other factors.

Very little is known about the direct effect the fluoride ion will have on the bondline durability considering the amounts generally present on the surface. Most likely this ion will be present as the AlF_3 compound which is generally stable and not very water soluble. One study (Reference 44) has observed changes in the net surface charge of hydrous aluminum oxides, and another (Reference 45) reports on the effect this ion has on the microstructure of the oxide layer.

The amount of phosphorous (as PO_4 anions) in the oxide layer of the alloys studied is small and apparently located on the outermost surface. Its effect is unknown at present; however, it is suggested that the effect should be positive when reference is made to all of the data on phosphate coatings and corrosion protection.

Zinc appears to be electrochemically neutral with reference to aluminum. If anything, the pitting potential of aluminum is decreased when alloyed with zinc (Reference 38). No definitive data has been presented for this element in the bondline of 7075 adhesively bonded structures.

SECTION V
CONCLUSIONS

Results from anodization studies on pure aluminum and clad aluminum alloys cannot be used as a data base for programs where bare aluminum alloys are going to be used. Elements added for alloying purposes will appear as microconstituents in the alloy surface. The microconstituents will have a marked influence on the anodic oxidation process which will alter the physio-chemical properties of the oxide layer. Some of these effects can be observed as voids in the oxide layer and segregates at the oxide-metal interface. These inhomogenieties will directly influence the number of possible electrochemical breakdown sites in the oxide layer.

REFERENCES

1. J. Diggle, T. Downie, and C. Goulding, Chem. Rev., 69, 365 (1969).
2. L. Young, Anodic Oxide Films, Academic Press, N.Y., 1961, Chap. 16.
3. G. Wood, Oxide and Oxide Films, Vol. 2, M. Dekker Inc., N.Y., 1973, Chap. 3.
4. J. Diggle, Oxide and Oxide Films, Vol. 2, M. Dekker Inc., N.Y., 1973, Chap. 4.
5. F. Keller, G. Wilcox, M. Tosterud, and C. Slunder, Metals and Alloys, 10, 219 (1939).
6. L. Spencer, Metal Finishing, Mar, 53 (1969).
7. H. Eichner and W. Schowalter, Forest Products Laboratory, Report No. 1813, May 1950.
8. J. Menford, Adhesives Age, July 1974.
9. A. Bethune, SAMPE Journal, 11 #3, 4 (1975).
10. A. Smith, J. Electrochem. Soc., 120, 1551 (1973).
11. R. Wegman, Picatinny Arsenal Tech. Rept. 4185, Picatinny Arsenal, Dover, N.J., March 1971.
12. C. Chang, Surface Sci., 25, 53 (1971).
13. G. Kammlott, Surface Sci., 25, 120 (1971).
14. F. Karasek, Research/Development, January, 25 (1973).
15. R. Walton, Plating, March, 219 (1972).
16. N. Rodgers, U.S. Patent 3,414,489, Dec. 3, 1968.
17. P. Bijlmer, Metal Finishing, Apr., 30 (1972).
18. J. Kape, Plating, January, 26 (1968).
19. L. Campanella, Plating, June, 575 (1972).
20. K. Wefers and G. Bell, Alcoa Research Laboratories Technical Paper #19, 1972.
21. R. Harrington and H. Nelson, Trans. Amer. Inst. Met. Eng., 137, 128 (1940).

REFERENCES (CONTINUED)

22. W. Vedder and D. Vermilyea, Faraday Soc. Trans., 65, 561 (1969).
23. R. Alwitt, Oxides and Oxide Films, Vol. 4, M. Dekker Inc., N.Y., 1976, Chap. 3.
24. G. Wood, J. O'Sullivan and B. Vaszko, J. Electrochem. Soc., 115, 618 (1968).
25. N. McDevitt, W. Baun, and J. Solomon, AFML-TR-75-122, Wright-Patterson AFB, Dayton, Ohio, November 1975.
26. N. McDevitt, W. Baun, and J. Solomon, AFML-TR-76-13, Wright-Patterson AFB, Dayton, Ohio, Marcy 1976.
27. T. Sun, J. Chen, and J. Venables, Appl. Surf. Sci., 1, 202 (1978).
28. J. Smith and W. Martinsen, Am. Cer. Soc. Bull., 52, 855 (1973).
29. G. Kissin, The Finishing of Aluminum, Reinhold Pub. Corp., N.Y., 1963, Chap. 2.
30. J. Solomon and D. Hanlin, Appl. Surf. Sci., in press.
31. N. McDevitt, W. Baun, G. Fugate, and J. Solomon, AFML-TR-77-55, Wright-Patterson AFB, Dayton, Ohio May 1977.
32. J. Zahavi, A. Zangvil, and M. Metzter, J. Electrochem. Soc., 125, 438 (1978).
33. N. McDevitt and W. Baun, AFML-TR-76-74, Wright-Patterson AFB, Ohio, June 1976.
34. W. Mackintosh, F. Brown, and H. Plattner, J. Electrochem. Soc., 121, 1281 (1974).
35. H. Strehblow, C. Melliar-Smith, and W. Augustyniak, J. Electrochem. Soc., 125, 915 (1978).
36. R. Bador, M. Romand, and G. Bouyssoux, 19th Colloquium Spectros. Internst., Philadelphia, PA., Nov 1976, Abs #203.
37. I. Muller and J. Galvell, Corros. Sci., 17, 179 (1977).
38. I. Muller and J. Galvell, Corros. Sci., 17, 995 (1977).
39. F. Mansfeld and J. Kenkel, Corros. Sci., 15, 183 (1975).

REFERENCES (CONTINUED)

40. F. Mansfeld and J. Kenkel, *Corros. Sci.*, 15, 239 (1975).
41. N. McDevitt, W. Baun, and J. Solomon, *J. Electrochem. Soc.*, 123, 1059 (1976).
42. G. Wood, W. Sutton, J. Richardson, T. Riley, and A. Malherbe, *Corrosion, NACE*, 526 (1974).
43. N. McDevitt, W. Baun, and J. Solomon, AFML-TR-78-128, Wright-Patterson AFB, Dayton, Ohio, September 1978.
44. S. Rajan, *Nature*, 262, 45 (1976).
45. J. Chen, T. Sun, J. Venables, and R. Hopping, *SAMPE Journal*, July/August 1978.
46. W. Baun, AFML-TR-79-4132, Wright-Patterson AFB, Ohio, September 1979.