NATIONAL BUREAU OF STANDARDS REPORT

10 346

SUMMARY REPORT OF TECHNICAL ADVISORY COMMITTEE STUDY OF THE ADHERENCE OF PORCELAIN ENAMEL ON ALUMINUM

August 1, 1966 – July 30, 1970

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards [1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics [2]—Radio Engineering [2]—Time and Frequency [2]—Astrophysics [2]—Cryogenics.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

Engineering Standards—Weights and Measures — Invention and Innovation — Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

Reactor Radiation—Linac Radiation—Nuclear Radiation—Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information — Computer Services — Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Located at Boulder, Colorado 80302.
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
421.04 – 4216371	September 28, 1970	10 346

SUMMARY REPORT OF TECHNICAL ADVISORY COMMITTEE STUDY OF THE ADHERENCE OF PORCELAIN ENAMEL ON ALUMINUM

August 1, 1966 – July 30, 1970

by
M. A. Baker
Porcelain Enamel Institute Research Associateship
National Bureau of Standards

Co Sponsored by the Ferro Corp.

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

TABLE OF CONTENTS

1. INTRODUCTION

The Porcelain Enameled Aluminum Council of the Porcelain Enamel Institute initiated a Research Associateship program at the National Bureau of Standards in 1966 to study the basic mechanisms of adherence of porcelain enamel to aluminum. It was felt that if the basic mechanisms of adherence were understood, then a test could be developed to accurately predict the spalling characteristics of any enamel-aluminum system.

This thorough understanding of adherence is important because spalling, the flaking or chipping of an enamel from the metal after exposure to weather, is the primary technical problem facing the porcelain enameled aluminum industry today.

This report summarizes the avenues investigated and presents a theory for the adherence of porcelain enamel to aluminum. The report is divided into four sections. The first section contains only background data-base metal and enamel compositions, pretreatments, and firing times for the enamel-metal systems studied. The second section contains research methods used to investigate the adherence of the enamel to the metal and discussion of the results obtained. The third section puts forth a theory of the mechanism of adherence of porcelain enamel to aluminum, and the forth section contains appendices which summarize the findings of this report relative to enamel-metal systems which spall and enamel-metal systems with good adherence. The findings in the appendices will be referenced to the sub-section numbers appearing in the left-hand margin of the second section of this report.

The terms "adherence" and "spall resistance" will be used interchangeably throughout this report. If an enamel-metal system has good adherence, it has good spall resistance, and conversely, if the system has poor adherence, it will have poor spall resistance and the enamel will flake away from the metal after being exposed to the weather.

1.1 BASE METAL

Four alloys were initially selected for study. These included two relatively pure alloys, 1199 and 1100, and two magnesium bearing alloys, 5257 and 5657. When the aforementioned alloys did not produce an enamel-alloy system that spalled readily, a magnesium disilicide alloy, 6061, and two high magnesium alloys, 5154 and 5086, were added. The compositions of the above alloys are given in Table 1.

Occasionally 3003, 5053 and 6063 alloys have been studied. The composition of the 6063 is given in Table 1 but the exact compositions of the 3003 and 5053 are not known. Also the initial lots of 6061 and 5086 have been depleted so the metal currently being used may vary slightly from the composition given in Table 1.

High purity magnesium was used for a study of the enamelability of magnesium and the rate of solution of magnesium oxide by the enamel.

Discussions of the effect of the different alloys of the adherence of the enamel to the metal will be covered later.

1.2 ENAMEL

The basic enamel used is a tan enamel with an A1-2 base frit. The oxide composition of this enamel, including mill additions, is given in Table 2.

There have been four variations of this enamel. The variation used most often has been designated "chrome-free". This enamel has titania substituted for the coloring oxide in the mill addition.

The other three variations are designated "alumina-rich", "silica-rich", and magnesia-rich". These variations were produced by substituting aluminia, silica, or magnesia respectively for the titania in the mill addition.

1.3 METAL PRETREATMENT

The metal was prepared for enameling by one of the following pretreatments:

1. Prefiring: The metal is heated at 1000°F for ten minutes prior to enameling.

2. Chemical Clean, R-100: The metal is subjected to a non-inhibited chemical cleaner at 180°F for seven minutes, rinsed and deoxidized with the R-100 etch for ten minutes and rinsed before enameling.

3. Pickled: The metal is subjected to the chemical clean, R-100 etch, rinse, and a conversion chromate bath before enameling. Pickling is the pretreatment used in industry to produce enameled 6061 with good spall resistance.

4. Anodizing: The metal was anodized in sulfuric acid before enameling.

In the following discussions these pretreatments will be referred to as prefired, chemical clean, pickled or anodized.

A few of the alloys were prepared for enameling by washing with acetone and vapor depositing a thin layer of metal before enameling. This pretreatment will be referred to as "vapor _____", where the blank will be filled in with the metal deposited.

1.4 FIRING

The basic firing cycle is ten minutes at 1000°F. However, this cycle was varied by extending the firing time at 1000°F to 30, 90, 300, and 600 minutes and by lowering the firing temperature to 960 and 940°F for ten minutes. To avoid confusion about firing conditions, the firing time and temperature will be given in further discussions, tables and figures. If the firing time and temperature are not given, they will be ten minutes at 1000°F.

2. DISCUSSION OF RESEARCH TECHNIQUES

2.1 SPALL TESTING

2.1.1 There are two standard spall tests [1,2] used in the Porcelain enameled aluminum industry. One test immerses the specimen in a 5 percent ammonium chloride solution for 96 hours while the other immerses the specimen in a one percent antimony trichloride solution for twenty hours. A specimen fails when the enamel flakes from the edge in pieces at least one inch long by 1/8 inch wide or if it spalls from the interior surface in areas at least 1/8 inch in diameter.

2.1.2 All specimens prepared for use in this program have been spall tested in antimony trichloride. A summary of the general spall resistance of the enamel-metal systems studied is given in Table 3. Since the spall resistance of an enamel-metal system may vary, the spalling behavior of a particular set of specimens will usually be presented with the results of other analyses in this report.

2.1.3 The reactions that occur between prefired and enameled 5154 and the antimony trichloride spall test solution were observed with slow motion photography. Later viewing of this film indicated that reactions occur almost immediately - gassing and bubbling are much in evidence, a black precipitate is formed on the aluminum and tends to concentrate at the enamel-metal interface, and a white gelatinous material appears to form at the enamel-metal interface. The pressure caused by these reactions at the interface appears to cause the enamel to spall.

The following spall tests have been conducted to determine how a special pretreatment, enamel, alloy, or alloying constituent affected the spall resistance of a particular enamel-metal system:

2.1.4 1. The effect of vapor plating metals on different alloys. Magnesium was vapor plated on 1100 to determine its effect on adherence. The specimens were prefired after vapor plating and then enameled. Spall tests indicated that all specimens of 1100 with vapor deposited magnesium spalled. The greater the amount of magnesium on the specimen, the more spalling occurred. When chrome was vapor deposited over the previously vapor deposited magnesium on 1100, the resulting enamel-metal system had excellent adherence.

Improved spall resistance was noted when chrome was vapor deposited on 5086. However, the enamel still spalled enough to constitute failure. Vapor deposited copper and iron also improved the spall resistance but not as much as chrome.

2.1.5 2. The effect of the distribution of magnesium disilicide in 6063.

Duplicate specimens of 6063 that had been treated to put the magnesium disilicide in solid solution, submicroscopically precipitated, coarsely precipitated, and very coarsely precipitated were enameled and spall tested. There was some variation between the duplicate specimens, but the specimens with the coarsely precipitated Mg_2Si exhibited the most spalling in both cases while the submicroscopically precipitated Mg_2Si consistently showed good spall resistance. The other two types of Mg_2Si showed variable results between these two extremes. These results indicate that the form of Mg_2Si may effect the enamel's spall resistance.

2.1.6 3. The Spall Resistance of Magnesium

High purity magnesium was enameled after various pretreatments. The spall resistance of these specimens is summarized in Table 4.

2.1.7 4. Spall resistance of Silica-Rich, Aluminia-Rich, or Magnesia-Rich Enamels.

Silica, aluminia and magnesia were substituted respectively for the titania in the standard mill addition. When these enamels were applied to prefired 3003, they showed excellent spall resistance except the magnesium-rich enamel, which showed some fishscale type spalling.

2.1.8 There have been industry reports that spall testing ware after deforming it over a mandrel gave a better correlation of spall resistance with field experience than spall tests on flat ware. Therefore, a mandrel with radii varying from 1/8 to 7 inches was designed. A set of specimens was then spall tested. One half of the specimens was deformed over the mandrel before testing and the other half was tested flat as control specimens. The spall tests on these specimens were very similar (see Table 5). However, minor differences in spall resistance were readily apparent on the deformed specimens but were not noticed on the flat specimens. It is possible that the time required to run a spall test could be reduced if deformed specimens were used.

2.1.9 There were also industry reports of spalling after exposure to high humidity. The first investigation of spalling caused by humidty consisted of exposing prefired and enameled 5086 to 100 percent relative humidity at 100°F. After four months exposure to these conditions, no spalling had occurred. Then the water was inadvertently turned off, the humidity dropped and the temperature rose to 275°F. This change in test conditions caused the enamel to spall severely. Other attempts to produce this type of spalling on prefired 5086 after shorter exposure times included:

1. Exposure to 100 percent relative humidity for 48 hours at 100°F followed by exposure in an oven at 275°F for 24 hours. This resulted in slight spalling after three complete cycles. After six complete cycles, no additional spalling had occurred.

2. Immersion in distilled water at room temperature for 48 hours followed by exposure in an oven at 275°F for 24 hours. This resulted in a very small amount of spalling after the third immersion-dry cycle and additional slight spalling occurred during the 6th cycle.

3. Total immersion in hot (170°F) water for 24 hours followed by 12 hours dry at 275°F in an oven. This resulted in spalling during the hot water part of the first cycle. Some additional spalling occurred during the second cycle. A further cycle did not yield any more spalling. This method gave the most spalling of all the five methods tried, but it was not as severe as had occurred on the long term humidity exposure which prompted this work.

4. Suspension for 24 hours (with accompanying condensation) of the samples over an enclosed water bath with the water temperature at 170°F. This was followed by a 12-hour drying cycle at 275°F in an electric oven. This was run for four cycles with no spalling.

5. A "Cleveland" paint tester set with cycles of one hour condensation and one hour dry. This was run continuously for seven weeks with no spall failures occurring.

2.2 ANALYSIS OF SPALL TEST SOLUTIONS

2.2.1 The spent spall solutions were analyzed to gain insight into reactions that result in spalling. A qualitative analysis of distilled water, ammonium chloride and antimony trichloride spall solutions after prefired 1100, 6061, and 5086 had been tested revealed that the spent spall solutions contain appreciable amounts of magnesium when spalling occurred. This analysis also indicated that manganese, lead, silicon, and titanium also appeared in the spall solutions after spalling had occurred. (See Table 6 for a summary of these test results).

2.2.2 A quantitative analysis of the spent antimony trichloride spall solutions after samples of prefired 1100, 6061, and 5086 had been tested indicated that the solution in which the 1100 was tested contained 0.3 mg of magnesium, the 6061 contained 31 mg, and the 5086 contained 165 mg. Since the relative amounts of magnesium in the spall solutions correlated fairly well with the amount of spalling observed on the enameled samples, another quantitative analysis for magnesium and chromium was made using both pickled and prefired 1100, 3003, 6061, and 5086 in distilled water, ammonium chloride, and antimony trichloride spall test solutions. The spall solutions were also analyzed after prefired and pickled metal blanks were tested. A summary of these results are presented in Table 7. Although these results again indicated an increase in magnesium with increased spalling, determinations on the unenameled metal blanks indicated a similar increase. When the values for the blanks were subtracted from the values for the enameled samples there was no consistent increase in the chrome or magnesium content of the spall test solutions for the enamel-metal systems that spalled.

2.2.3 Analyses to determine whether the magnesium was released from the metal by the enamel mill liquor or by the heat associated with the firing process indicated that the heat treatment appeared to be responsible for releasing the magnesium to the spall solution.

2.3 OXIDE LAYER

The oxide layers that form naturally on aluminum alloys have been investigated in regards to thickness, composition and dissolution by the enamel.

2.3.1 The thickness of the naturally occurring oxide and the oxide layer resulting from a ten minute prefire were determined by three of the aluminum companies. Two of the companines measured the thickness of the oxide layer after removing it from the metal, while the third measured it in situ. The in situ determinations appeared to be affected by the base metal and are not included in the results in Table 8.

2.3.2 The magnesium content of the naturally occurring oxide layer and the oxide layer formed during prefiring were measured by two laboratories. The magnesium content of the oxide layer was found to increase markedly as the magnesium increased in the alloys. These results are presented in Table 9.

2.3.3 Since the naturally occurring oxide films and the prefired oxide films are extremely thin and difficult to measure, thick oxide films were formed by anodizing to study the behavior of the oxide films during enameling and firing. Although the thickness of the anodizing was varied, certain trends were evident. About 5000 angstroms of the oxide on the high-purity aluminum alloys were taken into solution by the enamel while the oxide layer on alloys containing magnesium or manganese remained the same or increased during enameling and firing as illustrated in Table 10. Since magnesium is the main alloying constituent in alloys that are difficult to enamel, pure magnesium was also anodized and enameled, and surprisingly, the pure magnesium was also taken into solution by the enamel.

2.4 LIGHT MICROSCOPY

Light microscopy, one of the original analytical tools used in metallurgy, has been used both to monitor the preparation of specimens for examination by electron microscope and electron microprobe and to observe the microstructure at the interface of many enamel-metal systems.

2.4.1 The observations with the light microscope include studies of the effect of different pretreatments on Mg_2Si, Mg_5Al_8, α Al-Fe-Si, and $FeAl_3$ second phase constituents. These studies indicated: 1) the enamel by itself attacked only Mg_2Si, 2) the R-100 plus enamel severely attacked the Mg_2Si and Mg_5Al_8 and slightly attacked the α Al-Fe-Si and $FeAl_3$, 3) the R-100 followed by the alkaline chrome and enamel attacked the Mg_2Si and Mg_5Al_8 about the same as the R-100 and enameling but the α Al-Fe-Si and $FeAl_3$ appeared to be protected from attack by the addition of alkaline chrome. It was also observed that the alkaline chrome appeared to prevent the enamel from coming in contact with the Mg_2Si and 4) Alkaline chrome and enameling showed only slight attack on the Mg_2Si and Mg_5Al_8 and no attack on the α Al-Fe-Si or $FeAl_3$.

2.4.2 A series of photomicrographs taken with polarized light showed an interesting phenomenon between specimens that spalled and those that did not spall. The photomicrograph of prefired, enameled 5154 (which spalled badly) showed a continuous black layer between the enamel and the metal. The photomicrograph of prefired, enameled 6061 (which also spalled but not as badly as the prefired 5154) showed a black layer between the enamel and the metal along approximately 70 percent of the interface. The photomicrographs of pickled and enameled and vapor chrome and enameled specimens (which did not spall) showed a black layer across approximately 50 and 20 percent respectively, of the interface and the sample of prefired 1100 (which also did not spall) had no black layer between the metal and the enamel. Thus there appears to be a "reaction" layer between the enamel and the metal that may contribute to the enamel's spalling if it constitutes more than 50 percent of the interfacial area.

2.4.3 Recent studies of prefired 5086, enameled and fired for ten hours corroborated the existence of a "reaction" zone. It was also found that this zone contained lead and Mg_2Si particles and a magnesium rich (brown) zone. Evidently, it was this magnesium-rich zone that we saw earlier.

2.4.4 The light microscope was also used to observe the interfacial areas of 1100, 6061, and 5086 after exposure to both antimony trichloride and amonium chloride spall test solutions. These observations indicated that the interfacial areas on the systems that spalled badly were readily attacked by the spall test solutions but the systems that did not spall showed little or no attack.

2.5 ELECTRON MICROSCOPY

2.5.1 Replica electron microscopy has been used extensively to study the interfacial area on spalling and non-spalling ceramic-metal systems. These studies have shown a very smooth transition from the enamel to the metal on the non-spalling alloys but a rough transition occurs between the metal and the enamel on the alloys that spalled. However, this difference was detected only after etching. The effects of many different etchants, including antimony trichloride were investigated and substantiated the above findings.

The amount of oxide solution (See Section 23) was monitored by replica electron microscopy methods.

2.5.2 Transmission electron microscopy has been used on only one set of enameled 6061 specimens. However, this set of micrographs shows a marked difference in the transition across the interface on the specimens that spall and those that do not spall. The interface on the systems that do not spall appears smooth from the metal to the enamel with a fairly wide intermediate zone while the systems that spalled showed a narrow band that appeared segregated from the enamel.

2.5.3 The scanning electron microscope has been used to observe the porcelain enamel-metal interface. These observations substantiated earlier findings with replica electron microscopy.

2.5.4 The scanning electron microscope was also used to examine the fracture-surface after the enamel was removed by direct-tension pulling. These studies indicated that the enamel pulled free from the metal only on prefired 5086. The other enamel-metal systems tested all left a glass-like layer on the enamel surface. This glassy layer appeared fairly porous for the enamel-metal systems that spalled.

2.6 ELECTRON MICROPROBE

The electron microprobe was used extensively (see Tables 11 & 12) to determine both the quantitative and qualitative distribution of elements, near the enamel-metal interface. The two goals of the probe studies were to determine what elements, if any, accumulate at the interface to cause or cure spalling and to determine if a diffusion zone existed between the metal and enamel.

2.6.1 The initial probes indicated a build up of magnesium at the interface of the systems that spalled. However, further studies showed this build up to be erratic and, in addition, there appeared to be a uniform build up of magnesium on some of the systems that did not spall. This led to further investigations to locate other elements that might be combining with the magnesium in the alloys where spalling did not occur. These investigations indicated that sodium and potassium were present with magnesium in the systems that did not spall but were absent from the systems that spalled.

2.6.2 The probe plots in Figure 3 indicate the effect of magnesium, sodium, and potassium on enamel-metal systems that do and do not spall, These data indicate a low background level of magnesium on the samples that did not spall as opposed to high magnesium background levels for the systems that did spall. (The starting alloy was the same for these five samples) Also, the potassium build up at the interface was greater than the sodium build up for the systems that did not spall while the sodium build up was greater or equal to the potassium build up on the systems that did spall.

2.6.3 When pure magnesium was enameled it was seen, Figures 4-6, that the potassium diffuses more readily into the magnesium than does the sodium.

2.6.4 There was no noticeable interaction between constituents of the enamel and the metal when the individual probe traces were observed, but overplotting this data resulted in some interesting observations. The overplotted data illustrated in Figures 7 and 8 indicates that there is a fairly wide interaction zone between the porcelain enamel and the 1100. This interaction zone between the 6061 is narrower than for the 1100 and practically non-existent between the enamel and the 5154. The spall resistance of these systems follows the same pattern: 1100 has excellent spall resistance, 6061 has intermediate spall resistance and 5154 has poor spall resistance. Thus, it appears that the amount of interaction between the enamel and the metal affects the spall resistance of the enamel-metal system.

2.7 MECHANICAL TESTING

2.7.1 PEI ADHERENCE TESTER

2.7.1.1 Prior to the initiation of this program, Laboratory G had mechanically deformed 3/8 inch enameled extrusions on the PEI adherence press. This set of specimens had the enamel varied to change the spall resistance of the system. The appearance of the deformed areas on these specimens indicated that these enamel-metal systems had good to poor adherence. The systems with good adherence had some fractures occurring within the glass while the systems with poor adherence the enamel was completely removed leaving bright metal. These results also correlated with the results of antimony trichloride test on these specimens.

2.7.2 DIRECT-TENSION PULLING TESTS

2.7.2.1 A direct-tension-pulling test has been investigated as a possible substitute for the spall test solutions in evaluating the adherence of porcelain enamel on aluminum. The instrument used was an "Elcometer Adhesion Tester" often referred to as a "button tester". The test consists of epoxying a button on the enamel surface and then pulling on the button until it is removed.

Preliminary tests on a set of enameled specimens indicated that the appearance of the "buttonhole" correlated better with spall resistance than did the psi required to remove the button. (See Table 13) The fractures resulting from buttons pulled from 1199 were all in the glass while the fractures occurring on prefired 5086 were at the surface of the metal. Pickled 5086 and both pickled and prefired 6061 fractures were between these two extremes. These visual observations are supported by measurements of the conductive surface of the button-holes with the PEI adherence meter. The 1199 has practically no conductive area while the prefired 5086 has the largest conductive areas.

2.7.2.2 These results indicate that the weakest area of the 1199-enamel system is well into the glass - perhaps at the edge of the relatively wide interaction zone between the enamel and the alloy. (See Section 2.6) The weakest area in the 6061 systems appears closer to the alloy again suggesting a narrower interaction zone while the 5086 systems often fracture right at the enamel-metal interface indicating a very narrow or perhaps non-existent interaction zone.

2.7.2.3 The enamel and metal sides of the tensile fracture on both prefired and pickled 6061 were examined with the electron microprobe probe attachment on the scanning electron microscope. This examination revealed that the composition on the enamel side of the fracture was the same whether the enamel was pulled from the pickled or the prefired 6061. However, the analysis of the metal side of the fracture showed a higher sodium to potassium ratio for the prefired 6061 than for the pickled 6061. This substantiated earlier probe findings that there is a greater potassium concentration at the enamel edge of the interaction zone on pickled and enameled 6061 than on prefired and enameled 6061. This study also indicated that the enamel-metal system is mechanically weak on the enamel side of the interaction zone.

3. THEORY FOR THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

The data obtained to date suggest that good adherence (good resistance to spalling) of porcelain enameled aluminum requires a chemical interaction between constituents of the enamel and the alloy. This interaction is illustrated by electron microprobe results (section 2.6) and by partial or complete solution in the enamel of the original oxide layer on the aluminum (section 2.3). The resulting relatively thick interaction zone is not subject to chemical degradation (section 2.5) and is mechanically stronger than the enamel (section 2.7). Magnesium is either absent from the interaction zone or is associated with enrichments of alkali metals, particularly potassium (section 2.6).

When adherence is poor (enamel spalls) the interaction zone contains a layer of reaction products. This reaction layer may contain magnesium in some form, frequently in large concentrations and there is no potassium enrichment associated with the magnesium (section 2.6). Lead and Magnesium silicide have also been observed in the reaction layer (sections 2.4 and 2.6). The reaction layer is susceptible to chemical degradation (section 2.4 and 2.5), and in mechanical tests, the layer either breaks itself or it breaks away from the metal surface. The formation of this reaction layer apparently inhibits the formation of a wide interaction zone that is necessary for good adherence. A simplified illustration of the interaction zones for systems with good and poor adherence is presented in figure 9.

Commercially pure aluminum generally has good adherence and a characteristically wide interaction zone without a layer of reaction products. Aluminum-magnesium alloys with poor adherence show the typical reaction layer in a narrower interaction zone. When chromium or its compounds is present on the surface of the aluminum-magnesium alloys, spalling is usually diminished but not eliminated. It is reasonable to suspect that the chromium either inhibits the formation of a reaction layer or enhances the formation of a wide interaction zone, or both. The function and mechanism for the effect of chromium are not clearly established. Aluminum-magnesium-silicon alloys may or may not spall depending on the metallurgical state of the alloy (section 2.1) and the condition of its surface before enameling (section 2.1 and 2.4). Here again, chromium plays an important role but is not the only factor.

There are currently three theories about the mechanisms of spalling. All three theories involve the reaction layer. The first two theories were formed after watching the spall solution ($SbCl_3$) attack an enamel-metal interface (section 2.1). These are 1) the reaction product formed between the enamel and the metal was dissolved, leaving the enamel unattached to the metal or 2) the two precipitates and the gas that formed build up enough pressure to force the enamel from the metal. The third theory merely suggests that the presence of a reaction layer in systems that spall may create stresses that become great enough during the heating and cooling cycles that occur in natural weathering to cause the enamel to spall from the metal.

Future research will be directed toward further defining the nature of the undesirable reaction layer; the factors in the metal, its surface treatment, and in the enamel that affect the formation of the reaction layer; and methods for preventing its formation and for enhancing the formation of the more desirable interaction zone.

USCOMM-NBS-DC

4. APPENDICES*

APPENDIX 4.1 SUMMARY OF FINDINGS RELATING TO EASILY SPALLED SYSTEMS

A. The interface is mechanically weak

1. Enamel is readily removed by direct-tension pulling (2.7.2.1)
2. Enamel is readily removed by deforming (2.7.1.1)

B. Etching solutions preferentially attack interface

1. In major cases, this can be observed by light microscope (2.4.4)
2. This can always be observed at high magnification with electron microscopes (2.5.1, 2.5.3)

C. Large concentrations of magnesium are sometimes found at the enamel-metal interface (2.6.1)

D. Oxide layer is not reduced in thickness (2.3.3)

E. Oxide layer is rich in magnesium (2.3.2)

F. Flakes fracture off with force in spall solution (2.1.3)

* The number in parenthesis at the end of a statement refers to the subsection of the report where this finding was discussed. These subsection numbers are found in the left-hand margins of section 2.

APPENDIX 4.2 SUMMARY OF FINDINGS RELATING TO NON-SPALLING SYSTEMS

A. Interface is strong -

1. Direct tension pulling tests fracture the system in the porcelain enamel (2.7.2.1)
2. Deformation tests fracture the system in the porcelain enamel (2.7.1.1)

B. Etching solutions do not show preferential attack at the interface (2.5.1)

C. Magnesium concentrations at the interface are associated with concentrations of alkali metals or are not existent (2.6.1)

D. Interaction zone at interface is thick (2.6.4)

E. Oxide layer reduced in thickness (2.3.3)

F. Potassium diffusion results in enrichments at or near the interface (2.6.2)

APPENDIX 4.3 GENERAL CONDITIONS RELATING TO ALL SYSTEMS

A. Elements in the metal other than magnesium are not diffused to the surface (2.3.2)

B. Various humdiity exposures, weathering tests, etc., have not produced accelerated spall failures which could be duplicated (2.1.9)

C. Elements dissolved by spall test solution rely more on the composition of the alloy being tested than on small differences in composition at the interface (2.2.1, 2.2.2)

5. ACKNOWLEDGEMENT

This report would not be complete without acknowledging the efforts extended by the Technical Advisory Committee of the Aluminum Council. This committee: comprised of representatives of the frit manufacturer - Ferro; the aluminum companies - Alcan, Alcoa, Kaiser, and Reynolds; and the porcelain enameled aluminum fabricators - H. H. Robertson and Porce Len: has guided the research reported herein and has assisted in much of the laboratory work.

6. REFERENCES

1. Antimony trichloride spall test for porcelain enameled aluminum; PEI Bulletin T-51, Porcelain Enamel Institute, 1968.

2. Spalling resistance of porcelain enameled aluminum; ASTM C 486, ASTM Book of Standards, Part 13, 1966.

7. ABRIDGED GLOSSARY

1. Adherence: The ability of an enamel to stay on the metal after firing and during exposure to weather or a spall test solution.

2. Interaction Zone: An area between the enamel and the metal that contains constituents of both the enamel and the metal.

3. Interfacial Area: The area between the metal and enamel. It contains the interaction zone and the reaction layer, if one is present.

4. Reaction Product: An element or compound formed between the enamel and the metal which apparently inhibits the formation of an interaction zone.

5. Reaction Layer: A layer between the enamel and the metal that contains the reaction product.

6. Spall: The flaking or chipping of the enamel from the metal.

Table 1. Composition of the Alloys used in this program.

Alloy	Alloying Constituents, percent											
	Al	Mg	Cu	Si	Fe	Zn	Mn	Cr	Ni	Ti	V	Ga
1199	99.992	-	0.0003	0.004	0.002	-	-	-	-	-	-	0.002
1100[a]	99.150	-	0.150	0.120	0.510	0.020	0.020	-	-	0.010	0.010	0.01
1100[b]	99.17	-	0.12	0.10	0.60	-	-	-	-	0.01	-	-
6061	97.57	0.85	0.24	0.59	0.43	0.06	0.05	0.17	-	0.04	-	-
6063	98.77	0.54	0.01	0.44	0.23	-	0.01	0.01	-	-	-	-
5257	99.532	0.28	0.02	0.04	0.07	0.02	0.005	-	0.003	0.02	0.01	-
5657	99.02	0.79	0.06	0.04	0.04	0.02	0.01	0.01	0.01	0.01		
5154	95.93	3.5	-	0.10	0.19	-	0.01	0.26	-	-	-	-
5086	95.18	3.89	0.02	0.10	0.22	0.01	0.48	0.09	0.01	0.01	-	-

[a] Aluminum supplied by Laboratory A

[b] Aluminum Supplied by Laboratory B

Table 2. Oxide Composition of the Enamel

Oxide	Weight Percent in Enamel
PbO	26.471
TiO_2	24.850
SiO_2	22.378
Na_2O	10.458
K_2O	3.667
BaO	3.224
Sb_2O_5	2.330
Li_2O	1.671
B_2O_3	1.406
Cr_2O_3	1.283
ZnO	0.991
Fe_2O_3	0.956
Al_2O_3	0.315

Table 3. Summary of Spall Test Results for Various Alloys

Alloy	Pretreatment	Spall Test Results
1199	Prefire	Pass
1199	Pickle	Pass
1100	Prefire	Pass
1100	Pickle	Pass
6061	Prefire	Fail
6061	Pickle	Pass
5086	Prefire	Fail
5086	Pickle	Fail
5657	Prefire	50% Failed
5154	Prefire	Fail
5154	Pickle	Fail
5257	Prefire	Pass

Table 4 Spall Resistance of Magnesium

Pretreatment	Spall Resistance
Prefire	Failed
Pickled	Passed
Vapor Chrome	Not Tested*
Anodized, Unsealed	Spontaneous**
Anodized plus vapor chrome	Spontaneous**
Anodized plus water seal	Spontaneous**
Anodized plus Sodiumdichromate Seal	Passed

* The enamel did not wet the metal so the specimen was not spall tested

** The enamel spalled immediately after firing, no spall test was needed.

Table 5. Comparison of Spall Test Results on Flat and Mandrel Deformed Specimens of Porcelain Enameled Aluminum

Alloy	Pretreatment	Firing Time (min.)	Firing Temp. (°F)	Rank of Spall Tested Specimens* Flat	Mandrel Deformed	Length of Spalled Area on Deformed Specimens (inches)
			Specimens passing the spall test			
1199	Prefired	10	1000	3.5	4	0.6
1199	Pickled	600	1000	3.5	2.5	---
6061	Pickled	10	1000	3.5	5	0.8
1199	Pickled	10	1000	3.5	1	---
1199	Pickled	10	940	3.5	2.5	---
6061	Pickled	600	1000	3.5	6	1.2
5086	Pickled	10	1000	9	10	2.7
1199	Prefired	10	940	9	7	1.5
			Specimens on the borderline between passing and failing the spall test			
6061	Prefired	10	940	9	8.5	1.8
6061	Prefired	10	1000	9	8.5	1.8
5086	Pickled	10	940	9	11	2.9
			Specimens failing the spall test			
1199	Prefired	600	1000	12	16	4.5
5086	Prefired	10	940	13	14	4.3
5086	Pickled	600	1000	14	12	3.9
6061	Pickled	10	940	15	15	4.4
5086	Prefired	10	1000	16	13	3.9
6061	Prefired	600	1000	17	17	4.5

* A rank of one indicates the best spall resistance, a rank of 17 indicates the worst spall resistance. When the same rank is given to two or more specimens, there was no noticable difference in spall resistance between the specimens.

Table 6. Summary of Qualatative Analyses of Spall Test Solutions

Element	Spall Test Solution									Percentage Occurring in:			
	Distilled Water			Ammonium Chloride			Antimony Trichloride						
	1100	6061	5086	1100	6061	5086	1100	6061	5086	1100	6061	5086	Enamel
Elements Occurring in Both the Enamel and the Metal													
Aluminum	f*	f	f	c	d	d	f	f	f	99.15	99.57	99.18	0.315
Chromium	b	b	b	-	b	a	c	d	d	-	0.17	0.09	1.283
Iron	-	e	d	-	b	a	e	e	e	0.51	0.43	0.22	0.956
Silicon	b	d	d	a	c	c	c	d	d	0.12	0.59	0.10	22.378
Titanium	?	d	d	-	b	c	b	c	c	0.01	0.04	0.01	24.850
Zinc	b	c	c	-	-	-	b	c	c	0.02	0.06	0.01	0.991
Elements Occurring Only in the Metal													
Copper	d	c	c	a	a	a	c	c	b	0.15	0.24	0.02	-
Magnesium	c	d	d	a	d	d	c	e	e	-	0.85	3.89	-
Magnagese	a	b	d	-	a	a	b	c	c	0.02	0.05	0.48	-
Nickel	a	e	c	-	-	-	b	b	b	-	-	0.01	-
Elements Occurring Only in the Enamel													
Boron	e	e	e	a	a	a	b	c	c	-	-	-	1.406
Barium	d	d	?	a	a	a	?	d	d	-	-	-	3.224
Sodium	b	e	d	-	?	a	c	d	d	-	-	-	10.458
Lead	?	e	e	?	c	d	c	e	e	-	-	-	26.471
Antimony	b	b	e	-	-	-	d	d	d	-	-	-	2.330
Elements Occurring in Neither the Enamel nor the Metal													
Silver	b	b	a	-	?	a	b	?	a	-	-	-	-
Calcium	d	d	a	a	a	a	a	a	a	-	-	-	-
Strontium	b	c	b	?	-	a	a	b	b	-	-	-	-
Spall Resistance	Exc.	Exc.	Poor	Exc.	Good	Fair	Exc.	Fair	V. Poor				

* Concentrations of elements given in the table are as follows: a=<0.001 percent, b=0.001-0.01, c= 0.01-0.1, d= 0.1-1.0, e= 1.0-10.0 and f= >10.

Table 7. Quantitative Analysis of Spall Test Solutions

Alloy	PREFIRED: Enameled Specimens Total Mg (mg)	Total Cr (mg)	% Bare Metal (spall)	Metal Blanks Total Mg (mg)	Total Cr (mg)	Change in Concentration Mg (mg)	Cr (mg)	PICKLED: Enameled Specimens Total Mg (mg)	Total Cr (mg)	% Bare Metal (spall)	Metal Blanks Total Mg (mg)	Total Cr (mg)	Change in Concentration Mg (mg)	Cr (mg)
Distilled Water Spall Test Solution														
1100	0.00	0.00	0	0.00	0.00	0.00	0.00	0.00	0.17	1*	0.00	0.04	0.00	0.13
3003	0.00	0.16	1*	0.00	0.04	0.00	0.12	0.00	0.14	1*	0.02	0.06	-0.02	0.08
6061	0.07	0.14	1*	0.72	0.04	-0.65	0.10	0.06	0.13	1*	0.00	0.06	0.06	0.07
6061X	0.00	0.01	0	0.94	0.00	-0.94	0.00	0.00	0.01	1*	0.00	0.00	0.00	0.00
5086	0.03	0.12	0	1.94	0.06	-1.91	0.06	0.15	0.02	1*	0.10	0.02	0.09	0.00
Ammonium Chloride Spall Test Solution														
1100	0.00	0.12	0	0.00	0.14	0.00	-0.06	0.00	0.08	1*	0.00	0.02	0.00	0.06
3003	0.00	0.01	3	0.00	0.00	0.00	0.01	0.00	0.13	2	0.00	0.08	0.00	0.07
6061	0.44	0.05	1*	0.78	0.04	0.34	0.01	0.59	0.07	4	0.08	0.04	0.51	0.03
6061X	2.39	0.02	2	2.52	0.06	-0.13	-0.04	2.00	0.07	1*	1.16	0.10	0.84	-0.03
5086	7.76	0.21	70	1.94	0.12	5.82	0.09	4.20	0.56	20	0.24	0.04	3.96	0.52
Antimony Trichloride Spall Test Solution														
1100	0.00	0.16	0	0.00	0.08	0.00	0.08	0.06	0.10	0	0.00	0.70	0.06	-0.60
3003	0.24	0.17	85	0.04	0.14	0.20	0.03	0.07	0.17	35	0.02	1.30	0.05	-1.13
6061	2.55	0.65	5	1.80	0.30	0.75	0.35	0.43	1.15	60	2.54	2.10	-2.11	-1.95
6061X	2.73	0.29	30	5.46	0.34	-2.73	-0.05	2.17	0.29	5	4.34	0.64	-2.17	-0.35
5086	17.81	0.33	100	9.12	0.28	8.69	0.05	16.51	1.65	100	10.90	1.16	5.61	0.49

*This percentage of bare metal occurred mostly at marks caused by pins on which the samples rested during firing.

6061X was a new lot of 6061 which spalled after pickling but had good adherence after prefiring.

Table 8. Summary of Oxide Thickness Measurements

Alloy	Thickness of Naturally Occurring Oxide Layer, Å		Thickness of Prefired Oxider Layer, Å	
	Laboratory B	Laboratory C	Laboratory B	Laboratory C
1100	160	190	220	297
6061	236	393	620	840
6063	220	420	340	527
5657	110	233	400	577
5154	224	813	490	1310

Table 9. Summary of Analyses for the Percentage Magnesium in the Oxide Layer Occurring on Aluminum Alloys

Alloy	Magnesium in Naturally Occurring Oxide Layer, Percent		Magnesium in Prefired Oxide Layer, Percent		Difference in Magnesium Content of Naturally and Prefired Oxide Layers, Percent	
	Lab. A	Lab. C	Lab. A	Lab. C	Lab. A	Lab. C
1199	0.02	---	0.02	---	0.00	---
1100	0.00	0.04	0.00	0.01	0.00	-0.03
6061	0.34	0.47	0.98	1.30	0.64	0.83
6063	0.00	0.06	0.51	0.83	0.51	0.77
5657	0.11	0.09	0.60	0.78	0.49	0.69
5154	0.37	0.78	1.34	1.64	0.97	0.86

Table 10. Summary of Oxide Solution Measurements on Anodized Aluminum and Magnesium

Specimen	Thickness of Anodized Layer Before Enameling (A)	Thickness of Anodized Layer After Enameling (A)	Change in Anodized Layer (A)
Aluminum Anodized in Sulfuric Acid			
1199	3,000	0,000	-3,000
1199	26,000	21,000	-5,000
1199 Alkali Chrome	9,000	4,000	-5,000
1199, Alumina-rich Enamel	28,000	23,000	-5,000
3003	15,000	16,000	1,000
5053	2,000	3,000	1,000
5053	20,000	22,000	2,000
5086(Alcoa 100)* Unsealed	25,000	27,000	2,000
5086(NaOH)* Unsealed	27,000	27,000	0,000
5086(NaOH)* Dichromate Sealed	26,000	28,000	2,000
5086(NaOH)* Vapor Chrome	28,000	29,000	1,000
Magnesium Anodized in Sodium Hydroxide			
Dichromate Sealed	15,000	13,000	-2,000

* Pre-anodizing treatment

Table 11. Summary of Quantative Electron Microprobe Traces

Alloy	Pretreatment	Firing Time (min.)	Element												Date	Lab
			Pb	Si	Mg	Al	Cu	Cr	Ti	Na	C	K	Fe	Ln		
1100	Chem.Clean	10	x	x	x	x									11/ 1/66	E
6061	Chem.Clean	10	x	x	x	x									11/ 1/66	E
5154	Chem.Clean	10	x	x	x	x									11/ 1/66	E
5154	Chem.Clean?	10			x		x	x							2/24/67	E
6061	Chem.Clean?	10			x		x	x							2/24/67	E
5657	Chem.Clean?	10			x		x	x							2/24/67	E
1100		10	x			x									9/14/67	F
5154		10	x		x	x									9/14/67	F
5154		10			x											E
5154		10							x						5/10/68	C
6061		10			x				x						5/10/68	C
5154	Prefire	10			x	x				x						B
6061	Prefire	10			x	x				x						B
5086	Prefire	10			x										5/ 1/69	D
6061	Pickle	10			x										4/30/69	B
6061	Pickle	30			x										4/30/69	B
6061	Pickle	90			x										4/30/69	B
6061	Pickle	300			x										4/30/69	B
5086	Pickle	300			x						x				4/30/69	B
6061	Pickle	10			x							x			4/30/69	B
6061	Pickle	300			x							x			4/30/69	B
6061	Pickle	300			x					x					4/30/69	B
6061	Pickle	300			x					x					4/30/69	B
5086	Prefire	300			x					x		x			4/30/69	B
5086	Pickle	300			x					x		x			4/30/69	B

Table 11. (Cont.) Summary of Quantative Electron Microprobe Traces.

Alloy	Pretreatment	Firing Time (min.)	Element												Date	Lab
			Pb	Si	Mg	Al	Cu	Cr	Ti	Na	O	K	Fe	In		
6061	Pickle	90			x											D
H.P. Mg	Prefired	10		x	x			x		x	x	x			9/17/69	A
H.P. Mg	Pickled	10		x	x			x		x	x	x			9/17/69	A
H.P. Mg	Anodized, Dichromate Sealed	10		x	x			x		x	x	x			9/17/69	A
6061	Pickled	10			x			x		x		x			4/13/70	D
6061	Prefired	10			x			x		x		x			4/13/70	D
6061	Pickled	600			x			x		x		x			4/13/70	D
6061	Prefired	600			x			x		x		x			4/13/70	D
6061	Pickled	10(940°)		x	x			x		x		x	x	x	4/13/70	D
6061	Prefired	10(940°)		x	x										4/13/70	D

Table 12. Summary of Qualitative Electron Microprobe Scans.

Alloy	Pretreatment	Firing Time (min.)	Element												Date	Lab
			Mg	Na	Al	Cu	Zn	Pb	Ti	Cr	Fe	Si	O	S	K	
6061	Prefire	10	x	x	x	x	x	x	x	x	x	x	x			3/20/68	B
5154	Prefire	10	x	x	x	x	x	x	x	x	x	x	x			3/20/68	B
5086	Prefire	600	x		x							x				5/ 1/69	D
5086	Pickle	600			x							x				5/ 1/69	D
6061	Pickle	600	x													5/ 1/69	D
6061	Prefire	600	x													5/ 1/69	D
5086	Pickle	10	x		x				x							5/ 1/69	D
5086	Pickle	30	x		x				x							5/ 1/69	D
5086	Pickle	90	x		x				x							5/ 1/69	D
5086	Pickle	300	x		x				x							5/ 1/69	D
5086	Prefire	10	x		x				x							5/ 1/69	D
5086	Prefire	30	x		x				x							5/ 1/69	D
5086	Prefire	90	x		x				x							5/ 1/69	D
5086	Prefire	300	x		x				x							5/ 1/69	D
6061	Pickle	10	x		x				x							5/ 1/69	D
6061	Pickle	30	x		x				x							5/ 1/69	D
6061	Pickle	90	x		x				x							5/ 1/69	D
6061	Pickle	300	x		x				x							5/ 1/69	D
6061	Pickle	10	x							x						4/30/69	B
6061	Pickle	30	x							x						4/30/69	B
6061	Pickle	90	x							x						4/30/69	B
6061	Pickle	300	x							x						4/30/69	B
5086	Pickle	10	x							x						4/30/69	B
5086	Pickle	30	x							x						4/30/69	B
5086	Pickle	90	x							x						4/30/69	B
5086	Pickle	300	x							x						4/30/69	B

Table 12, (cont.) Summary of Qualatative Electron Microprobe Scans.

Alloy	Pretreatment	Firing Time (min.)	Element													Date	Lab
			Mg	Na	Al	Cu	Zn	Pb	Ti	Cr	Fe	Si	O	S	K		
5086	Prefire	10	x													4/30/69	B
5086	Prefire	30	x	x											x	4/30/69	B
5086	Prefire	90	x													4/30/69	B
5086	Prefire	300	x	x											x	4/30/69	B
6061	Pickle	10	x														D
6061	Pickle	90	x														D
6061	Prefire	10	x														D
6061	Prefire	90	x														D
6061	Prefire,R-100 Prefire	10	x														D
6061	Prefire,R-100 Prefire	90	x														D
6061	Prefire	10(940°)	x									x				4/13/70	D
6061	Pickle	10(940°)								x						4/13/70	D
6061	Prefire	10	x													4/13/70	D
6061	Prefire	600	x													4/13/70	D
6061	Pickle	600	x													4/13/70	D
6061	Prefire	10(940°)	x													4/10/70	B
6061	Pickle	10(940°)	x													4/10/70	B
6061	Prefire	10	x													4/10/70	B
6061	Pickle	10	x													4/10/70	B
6061	Prefire	600	x													4/10/70	B
6061	Pickle	600	x													4/10/70	B
6061	Prefire	10			x			x	x					x	x	7/20/70	E
6061	Pickle	10						x								7/20/70	E

Table 13. Summary of Button Test Results

Pretreatment	Firing Time (min)	Firing Temp (°F)	PSI Required to Pull Button			PEI Adherence Meter Counts		
			1199	6061	5086	1199	6061	5086
Pickled	600	1000	340	430	100	1.1	7.7	21.3
Prefired	600	1000	370	400	300	1.0	6.1	67.0
Pickled	10	1000	360	370	460	0.3	3.8	0.5
Prefired	10	1000	360	360	650	0.3	6.1	7.6
Pickled	10	940	310	440	400	0.3	9.1	8.7
Prefired	10	940	320	400	520	1.6	6.3	14.1

Figure 1. Enameled 1100, (good adherence), etched with 5% NaOH, 8 kX

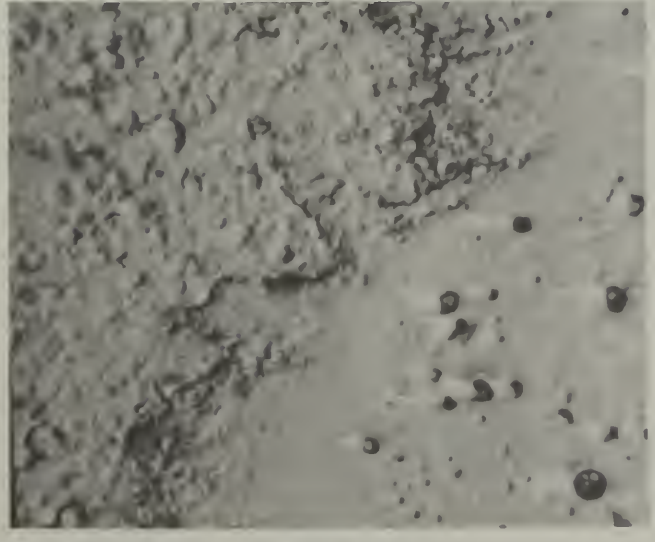
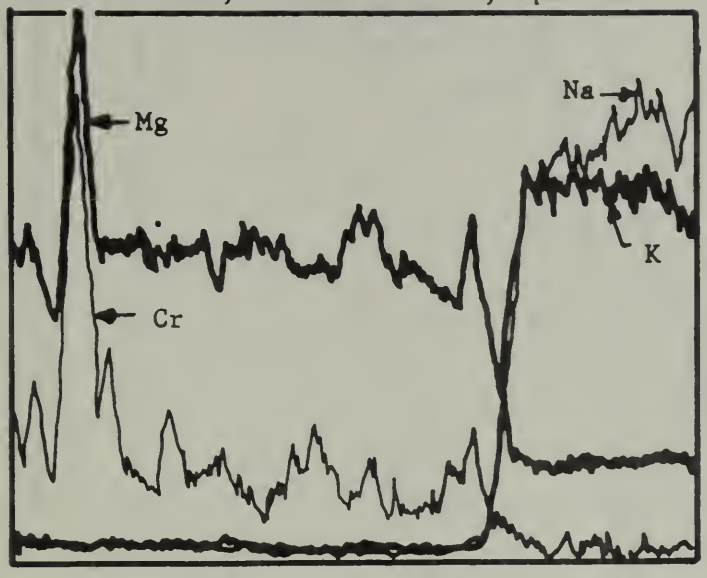


Figure 2. Enameled 5154, (poor adherence), etched with 5% NaOH, 8 kX

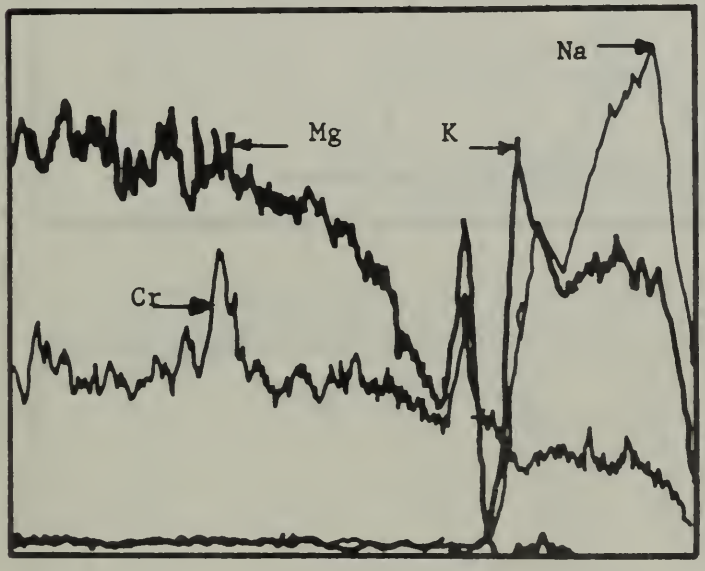
Pickled 6061, 10 min. at 940, Spalled



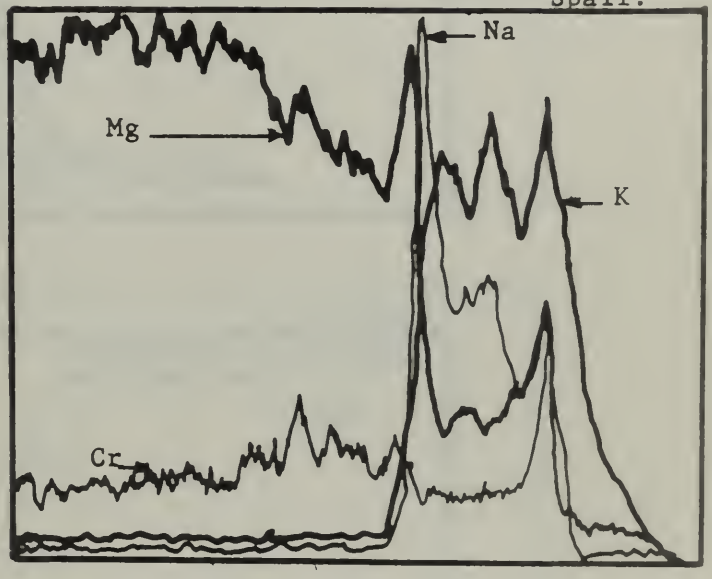
Metal

Enamel

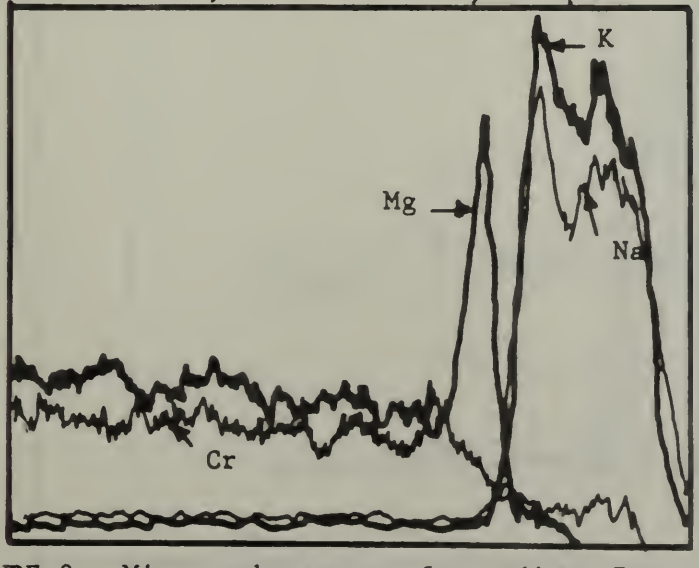
Pickled 6061, 10 min. at 1000, No Spall



Prefired 6061, 10 min. at 1000, Borderline Spall.



Pickled 6061, 10 hr. at 1000, No Spall



Prefired 6061, 10 hr. at 1000, Spalled

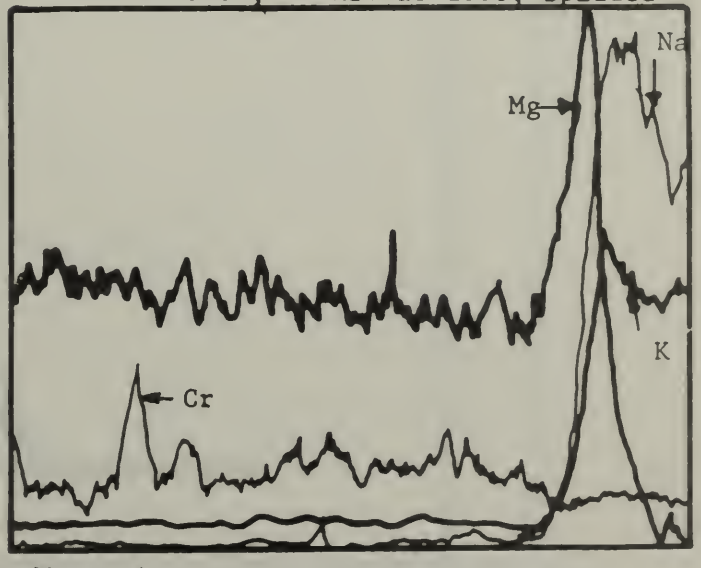


FIGURE 3. Microprobe traces for sodium, Pottasium, Magnesium and Chromium on 6061 with various pretreatments and firing conditions.

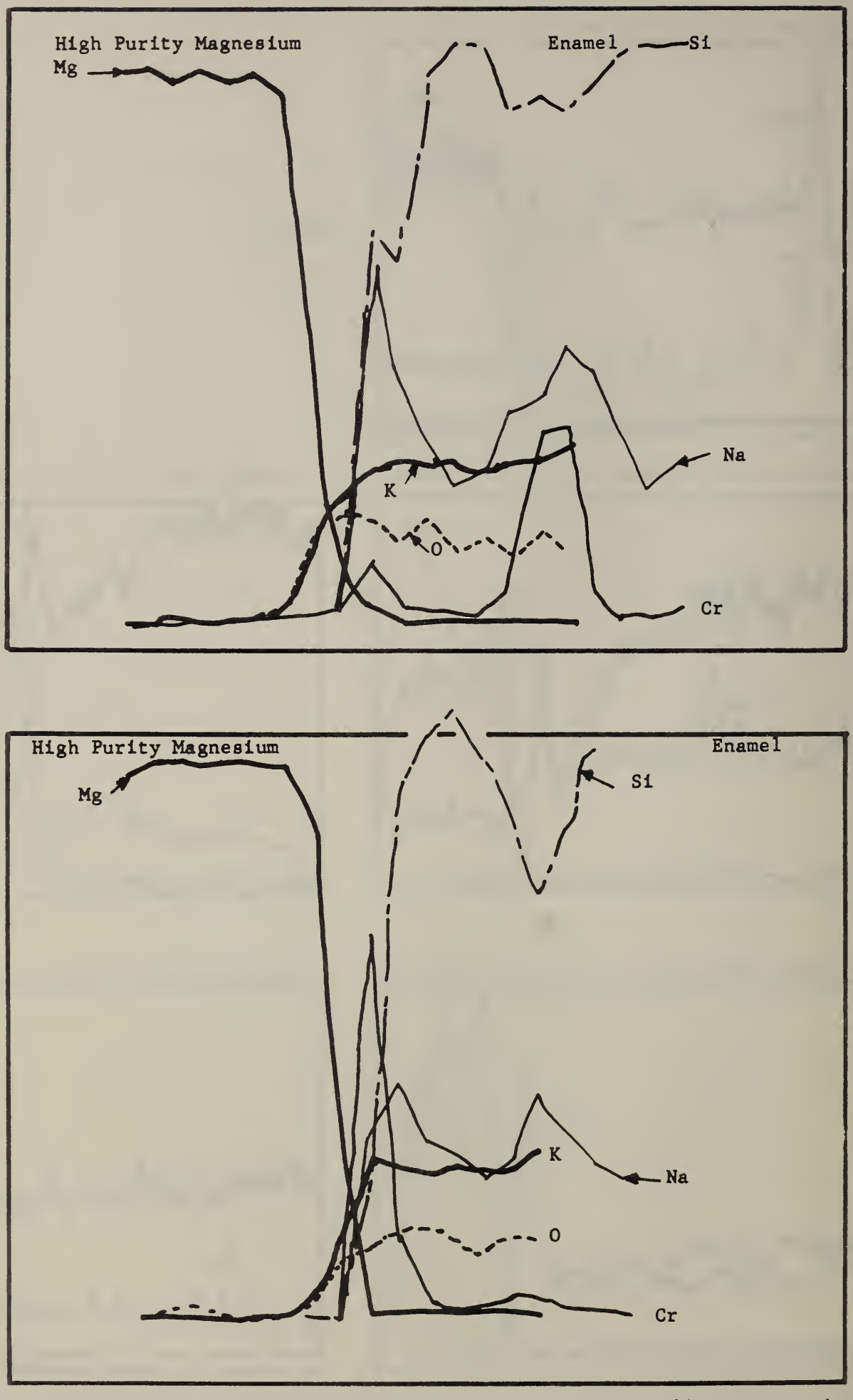
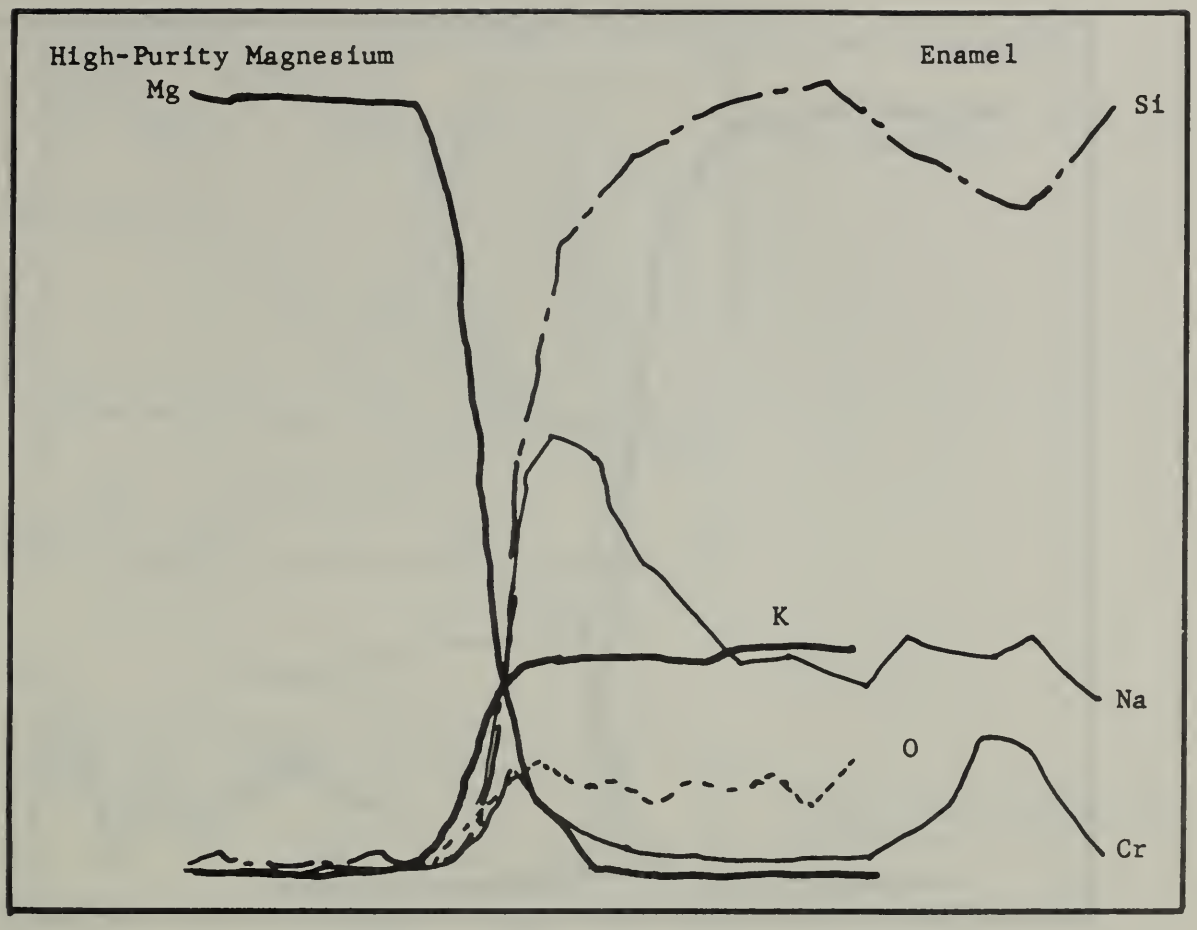


FIGURE 4. Microprobe traces for sodium, chromium, potassium, silicon, magnesium, and oxygen on anodized, dichromate sealed, enameled, high-purity magnesium. Not the diffusion of the potassium into the magnesium. This system did not spall.



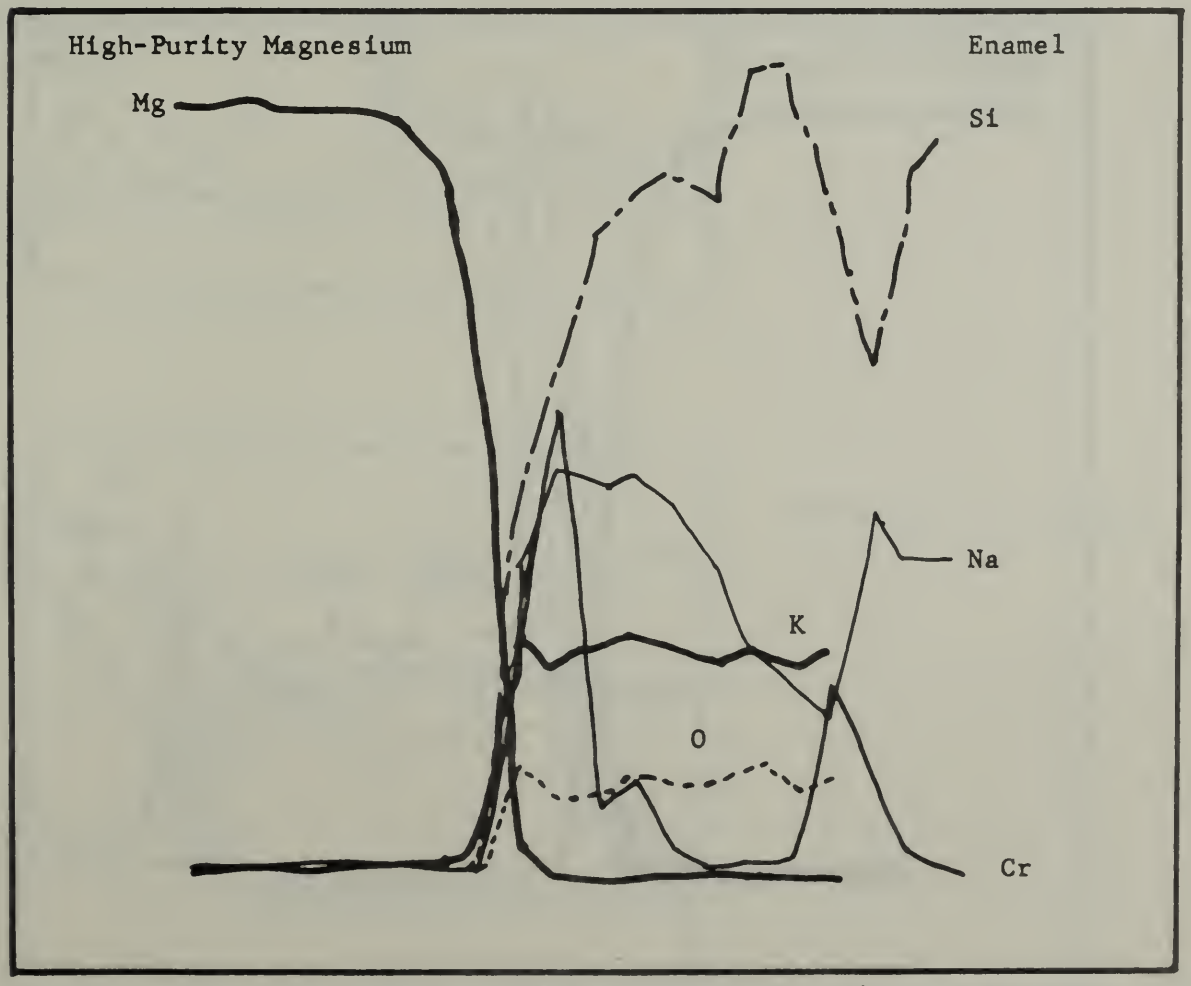


FIGURE 5. Microprobe traces for sodium, chromium, potassium, silicon, and oxygen on pickled, enameled, high-purity magnesium. Note the diffusion of the potassium into the magnesium in the top set of traces. This system did not spall.

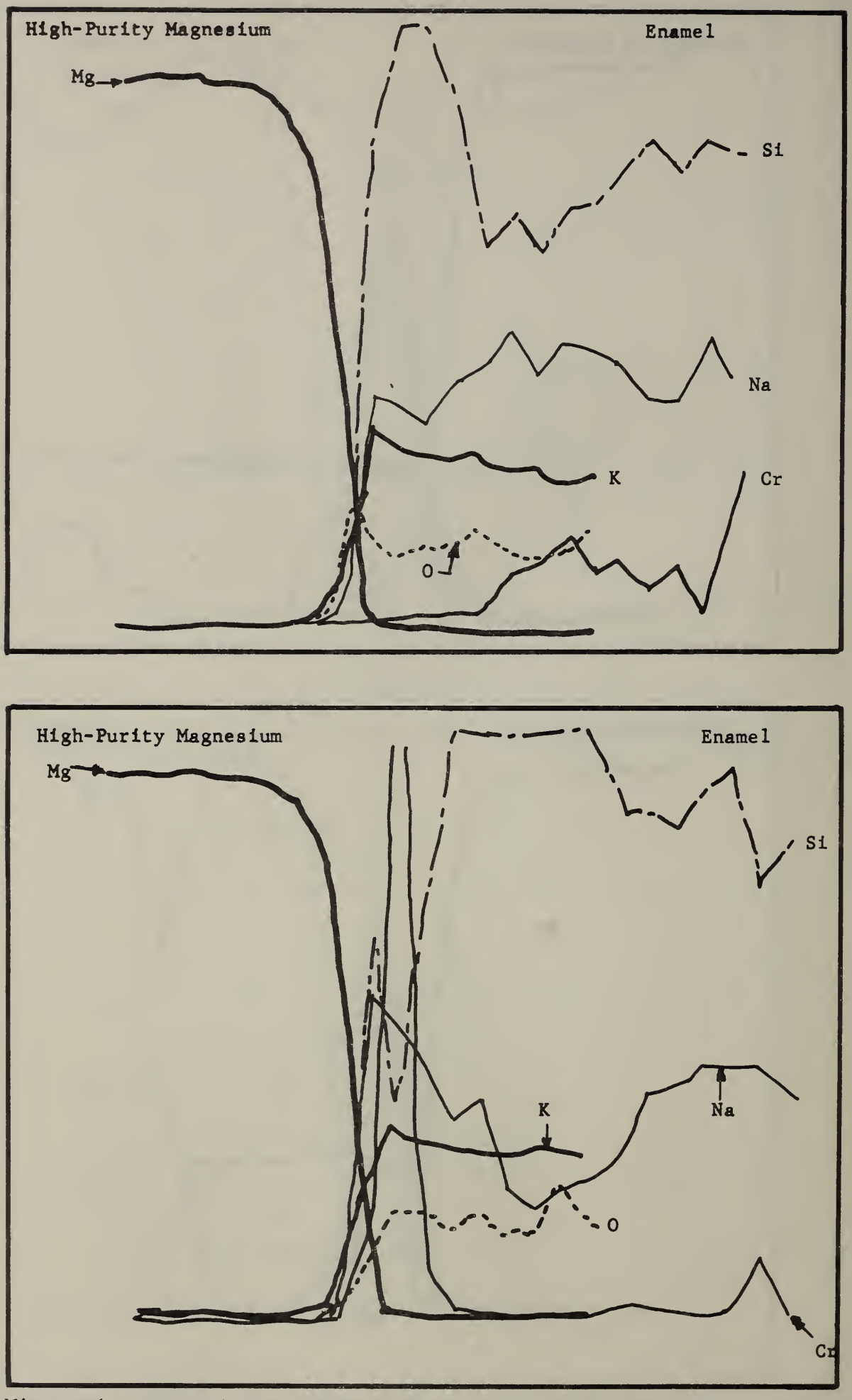
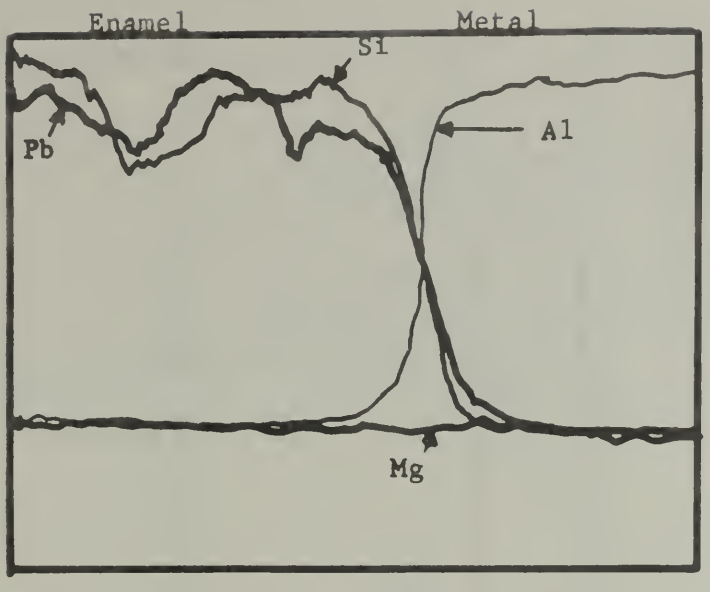
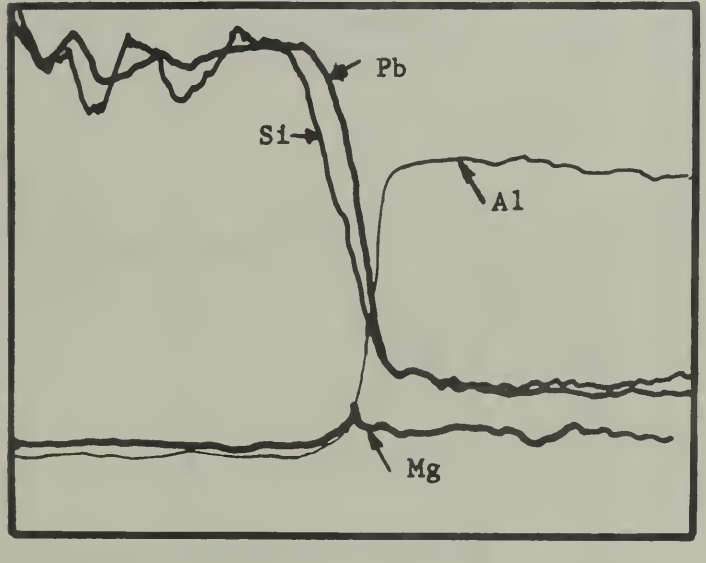


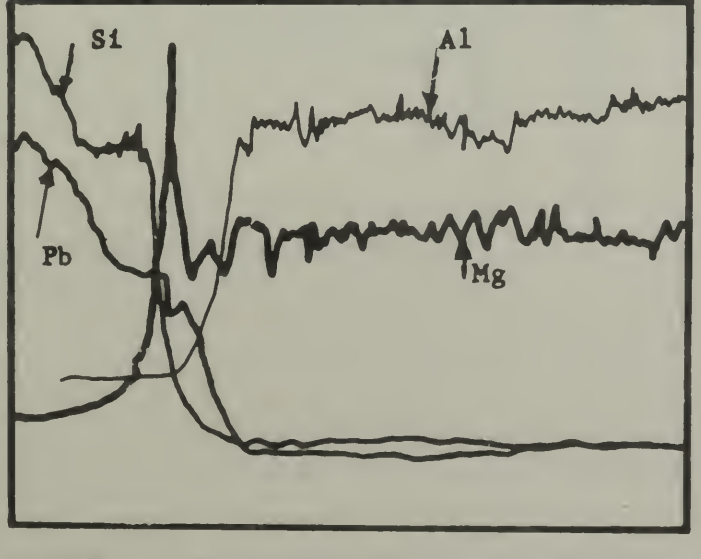
FIGURE 6. Microprobe traces for magnesium, sodium, potassium, oxygen and chromium on prefired, enameled, high-purity magnesium. This system spalled about ten percent. Note the simularity in diffusion between the potassium and the sodium into the magnesium.



Chemically Cleaned 1100,
No Spalling

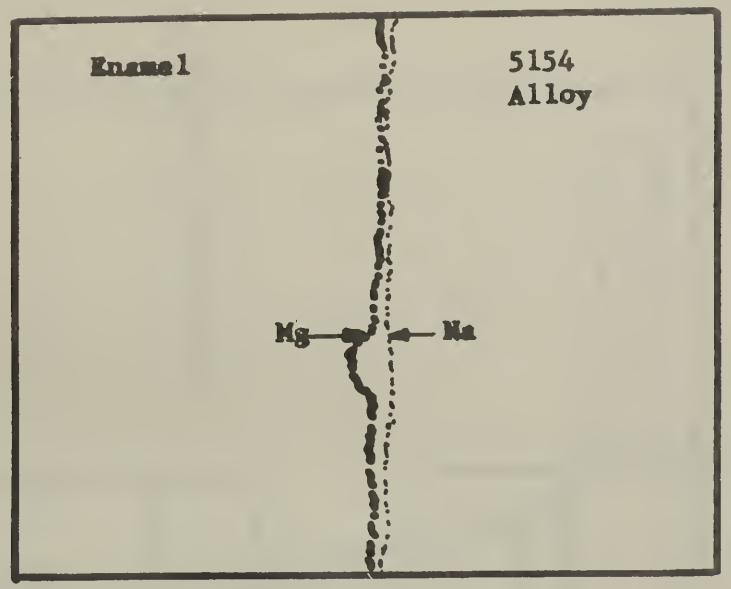


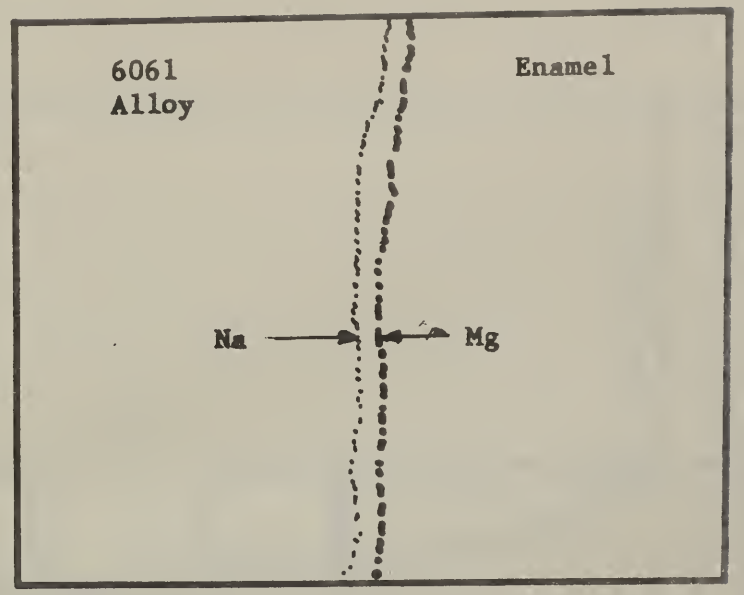
Chemically Cleaned 6061,
Borderline Spall

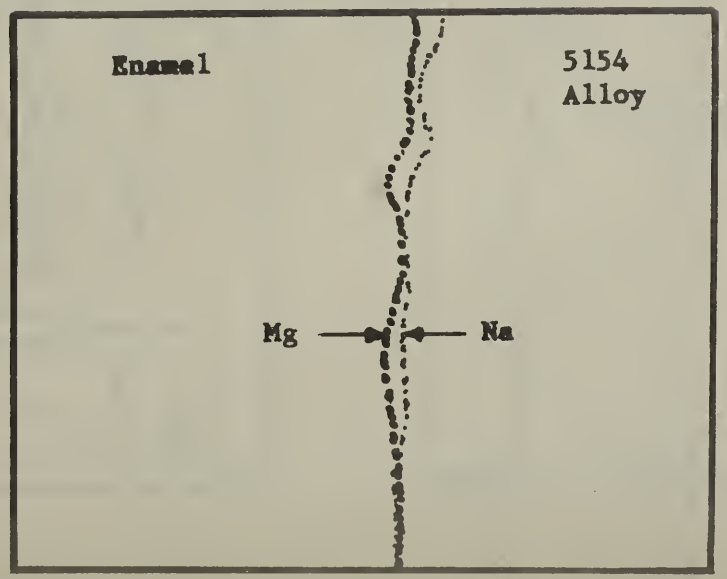


Prefired 5154, Spalled

FIGURE 7. Microprobe Traces for Silicon, Lead, Aluminum and Magnesium on 1100, 6061, and 5154.







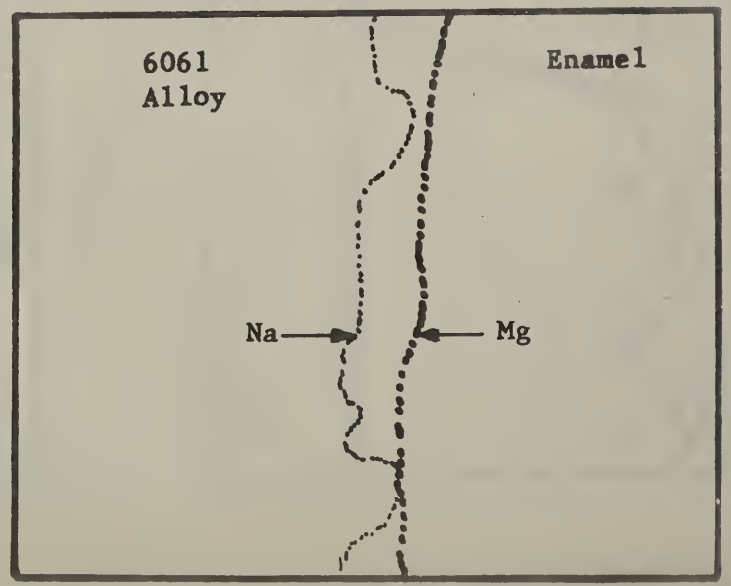


FIGURE 8. Overplotted microprobe scans showing the edge of the Magnesium and Sodium Concentrations. Note the narrow diffusion zone between the 5154 and enamel - a system that spalls - and the widediffusion zone between the 6061 and the enamel - a system with good adherence.

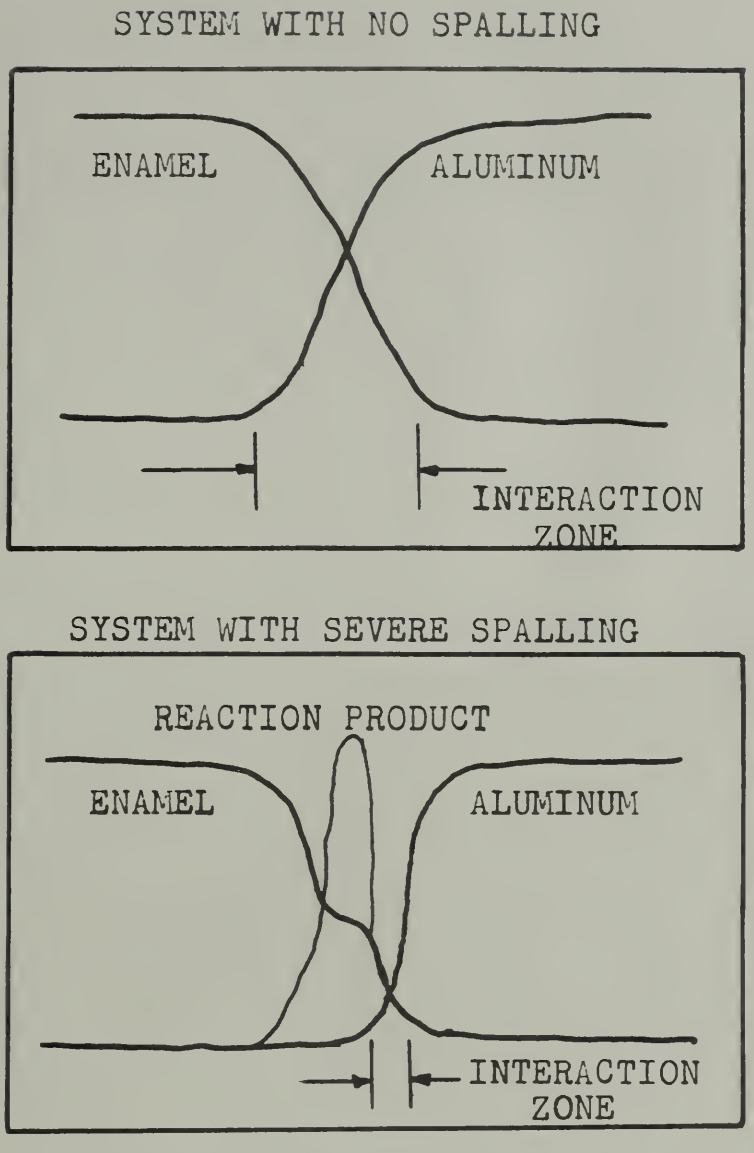


Figure 9. Schematic drawing of microprobe traces showing the differences in the width of the interaction zones for enamel-metal systems with varing degrees of spall resistance.


DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS