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The Adherence of Porcelain Enamel to Aluminum

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The Adherence of Porcelain Enamel to Aluminum

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ABRIDGED GLOSSARY

1. Adherence: The ability of an enamel to stay on the metal after firing.

2. Diffusion Zone: An area between the porcelain enamel and the aluminum alloy that contains constituents of both the enamel and the alloy.

3. Reaction Product: An element or compound formed as a result of reaction between the enamel and the metal.

4. Spalling: The flaking or chipping of the enamel from the metal. In this paper, spalling is the result of exposure to a chemical or natural weathering environment, not of mechanical damage.

5. Porcelain Enamel: A glass coating that is fused to a metal at temperatures of 900°F or higher. In this paper "enamel" and "porcelain enamel" will be used interchangeably.

6. Frit: The basic glass used in the porcelain enamel.

7. Mill Additions: Opacifiers, coloring oxides, and suspending media that are added to the frit to give the porcelain enamel the desired finished appearance and to make it easy to apply to the base metal.

8. Firing: The heating of the metal and applied enamel to fuse the enamel to the metal.

9. Transmission Electron Microscopy: A beam of electrons is passed through the specimen being studied. Differences in the absorption of the electrons are shown on a fluorescent screen or photographic film.

10. Replica Electron Microscopy: The same as transmission electron microscopy except a replica is made of the surface to be studied which eliminates the need for preparing extremely thin specimens.

11. Scanning Electron Microscopy: A beam of electrons is reflected off the surface being studied. This enables one to study thick specimens without preparing replicas.

12. Electron Microprobe: The specimen is bombarded with an electron beam, which causes it to emit X-rays characteristic of the elements present. These X-rays are either displayed to give a qualitative indication of the distribution of the element or they can be calibrated to give a quantitative distribution of the element.

13. X-ray Powder Diffraction: The material to be studied is finely ground (powdered) and then irridated with X-rays from a given source. The elements present in the powder can then be identified by their characteristic peaks.

METRIC/CUSTOMARY UNIT CONVERSIONS

A. Temperature

1000°F	538°C
960°F	516°C
940°F	504°C
275°F	135°C
170°F	77°C
100°F	38°C

B. Weight

2000 lbs.	908 Kg

C. Length

Angstroms	1×10^{-10} meters
Inch	2.54 centimeters

TABLE OF CONTENTS

The Adherence of Porcelain Enamel to Aluminum

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Light and electron microscopy, electron microprobe, and X-ray diffraction techniques were used to determine the mechanisms of adherence of porcelain enamel to aluminum. A theory is presented that adherence depends upon diffusion of aluminum into the enamel and further, the diffusion zone should be relatively free of reaction products for the enamel-metal system to retain good adherence after exposure to chemical solutions or to weathering. Round-robin testing of 6063 aluminum alloy extrusions indicated that this alloy can be enameled if care is exercised in the selection of the enamel and the pretreatment.

Key words: Adherence; aluminum; electron microprobe; electron microscope; porcelain enamel; spalling; X-ray diffraction.

INTRODUCTION

The Porcelain Enameled Aluminum Council of the Porcelain Enamel Institute (PEI) initiated a Research Associateship program at the National Bureau of Standards (NBS) in 1966 to study the mechanisms of adherence of porcelain enamel to aluminum. An understanding of adherence is important because spalling (or flaking of the enamel from the aluminum alloy some time after the finished product has been placed in service) is the primary technical problem facing the porcelain enameled aluminum industry.

It was felt that if the mechanisms of adherence and spalling were understood, then more of the commercially available aluminum alloys might be porcelain enameled. It would be beneficial to producers of porcelain enameled aluminum products if the aluminum alloys for porcelain enameling did not have to be specially ordered from the primary metal suppliers or if lighter gages of the higher strength aluminum alloys could be porcelain enameled without subsequent spall failures.

This 7 year research program is unique in that the research work was carried out in the laboratories of four cooperating aluminum companies and one frit company (see acknowledgment, Section 7) as well as the laboratories at NBS.

This report summarizes the avenues investigated and presents a theory for the adherence of porcelain enamel to aluminum. It also summarizes round-robin testing made to determine whether porcelain enamel could be successfully applied to 6063 aluminum alloy. This alloy was chosen because of its wide availability from both primary and secondary suppliers and its "easy squeeze" extrusion properties making it an ideal metal for such applications as window frames and door jambs.

This report contains 8 sections. Section 1 contains only general introductory information. Section 2 contains background information on base metal and enamel compositions, pretreatments and firing times for the enamel-metal systems studied. Section 3 describes research methods used to investigate the adherence of the enamel to the metal and the discussion of the results obtained. Section 4 puts forth a theory for the adherence of porcelain enamel to aluminum. Section 5 contains the results of the round-robin testing and Section 6 provides a summary of the findings resulting from this 7 year research program. Section 7 contains an acknowledgment to those companies that contributed to this program and Section 8 is a bibliography of reports on this project.

The base metal and enamel compositions or the pretreatment and firing data for the enamel-metal systems included in the round-robin tests are not reported in Section 2 because the processing of these specimens was done in commercial plants using proprietary procedures. Occasionally, in Section 3, the laboratories conducting the studies are referred to as laboratory A, B, C, etc. These designations refer either to the laboratories at NBS or to the research laboratories at one of the four aluminum companies or of the frit company cooperating in this work.

2. BACKGROUND INFORMATION

2.1 Base Metal

A total of 12 aluminum and a high purity magnesium alloys was used in the program. The four alloys initially selected for study 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 silicide alloy, 6061, and two high magnesium alloys, 5154 and 5086, were added. The compositions of these alloys are given in table 1.

Occasionally, 3003, 5053 and 6063 alloys have been studied in this work. The composition of the 6063 is given in table 1 but the exact compositions of 3003 and 5053 were not known. Also, the initial lots of 6061 and 5086 have been depleted so the metal used toward the end of this program may vary slightly from the composition given in table 1.

Super purity alloys (1199) with the additions of 1% Mg_2Si and 2% Mg were added late in the program. The composition of these alloys is also 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. Unless otherwise noted, all specimens were 3 x 6 inch rectangles cut from sheet stock.

2.2 Enamel

The basic enamel used was a tan enamel with an AL-2* frit. The oxide composition of the fired enamel, including the frit and mill additions, is given in table 2.

There have been four variations of this enamel. The variation used most often has been designated "basic white lead-silicate enamel". This enamel had titania substituted for the coloring oxide in the mill addition. The oxide composition of the frit (AL-2) used in the "basic white lead-silicate enamel" is given in table 3.

The other three variations are designated "alumina-rich", "silicate-rich", and "magnesia-rich". These variations were produced by substituting alumina, silica, or magnesia respectively for the titania in the mill addition. The spall test results of the enamels did not warrant the determination of their fired compositions.

In addition to these four variations of the basic enamel, two special enamels were prepared for this test program. These were designated "Lead-Free" and "Silica-Free" enamels. The oxide compositions of the frits used in these special enamels are also presented in table 3.

2.3 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 Cleaning: The metal is subjected to a hot buffered alkaline cleaner before enameling.

*The AL-2 number indicates to industry members which of the many commercially available frits was used.

3. Pickling: The metal is subjected to the chemical clean plus a hot acid chromate deoxidizer, and an alkaline-chromate bath before enameling. Pickling as described above is the preferred pretreatment used in the industry to produce enameled 6061 alloy with good spall resistance.

4. Anodizing: The aluminum is anodized in sulfuric acid before enameling.

5. Vapor Deposition: A few of the alloys were prepared for enameling by washing with acetone and vapor depositing a thin layer of metal.

These pretreatments will be referred to as prefired, chemical clean, pickled, anodized or vapor deposited _____, where the blank will be filled in with the metal deposited.

2.4 Firing

The basic enameling firing cycle was ten minutes at 1000°F. However, the firing cycle was varired by extending the firing time at 1000°F, to 30, 90, 300, 480, 600, and 1080 minutes or by lowering thefiring temperature to 960 and 940°F for 10 minutes. To avoid possible 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. Except for the enamels in the round-robin tests, the firing was done in electrical laboratory furnaces.

The furnace atmosphere was varied from air at 760 mm Hg pressure to air at 193 mm Hg, nitrogen at 193 mm Hg, hydrogen (35%) - argon (65%) at 193 mm Hg, oxygen at 193 mm Hg, argon at 193 mm Hg, nitrogen at 0.003 mm Hg, and a mixture of nitrogen at 163 mm Hg plus 30 mm water vapor for the resulting atmosphere (nitrogen plus water vapor) at 193 mm Hg pressure. The furnace was also operated at 760 mm pressure with oxygen flowing through it during the firing cycle. Water was also added to asbestos mats placed in the furnace in amounts varying from 0 to 200 cc. This was thought to simulate changes in industrial furnaces atmospheres as the amount of ware through the furnace is increased.

3. DISCUSSION OF RESEARCH TECHNIQUES

3.1 Chemical Spall Testing

There are two standard chemical spall tests used in the porcelain enameled aluminum industry. For one test the specimen is immersed in a 5 percent ammonium chloride solution for 96 hours while for the other the specimen is immersed in a one percent antimony trichloride ($SbCl_3$) solution for 20 hours. There is no mechanical stress applied in either test. A specimen fails as a result of these chemical tests 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.

All specimens prepared for use in this program were spall tested in antimony trichloride and a summary of the general spall-resistance data is given in table 4. Since the measured spall resistance of a specific enamel-metal system may vary from specimen to specimen, the spalling behavior of a particular set of specimens will usually be presented with the results of other tests in this report. Some additional spall tests using distilled water and ammonium chloride were also run.

The reactions that occurred 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 occurred almost immediately - gassing and bubbling were much in evidence, a black precipitate was formed on the aluminum surface and tended to concentrate near the enamel-metal interface. A white gelatinous material also appeared to form near the enamel-metal interface. The pressure caused by these reactions at the interface apparently caused the enamel to spall. The time required for these reactions to cause spalling was less than five minutes.

Additional studies of the action of antimony trichloride on polished sections of number 6061 alloy indicated that the $SbCl_3$ spall test solution attacked the aluminum at specific sites, such as at certain Mg_2Si and at αAlFeSi particles and at certain grain boundaries.

3.1.1 Effects of Pretreatments, Enamel, Alloy or Alloying Constitutents on Spall Resistance

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

1. The effect of vapor deposition of metals on spall resistance of various alloys.

Magnesium was vapor deposited on number 1100 alloy, prefired and then enameled. All specimens of 1100 with vapor-deposited magnesium spalled during the spall tests. The greater the amount of magnesium deposited on the specimen, the greater the spalling. When chromium was vapor deposited over the previously vapor-deposited magnesium on the resulting enamel-metal system had excellent spall resistance.

Improved spall resistance was noted when chromium was vapor deposited on number 5086 alloy (which contains about 4 percent magnesium). However, the enamel still spalled enough to constitute failure. Vapor-deposited copper and iron also improved the spall resistance of 5086 but not as much as chromium.

2. The effect of the distribution of magnesium silicide on the spall resistance of number 6063 alloy.

Four sets of duplicate specimens of 6063 alloy were heat treated to put its magnesium disilicide component into four forms: solid solution, submicroscopically precipitated, coarsely precipitated, and very coarsely precipitated. These specimens were then pickled, 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 specimens while the submicroscopically precipitated Mg_2Si consistently showed good spall resistance. The specimens with the other two forms of Mg_2Si showed variable results between these two extremes. These results indicate that the particle size of Mg_2Si may affect the enamel's spall resistance, possibly due to the ability of pretreatments to remove Mg_2Si from the surface of the specimen.

3. The spall resistance of magnesium.

High purity magnesium was enameled after various pretreatments. The spall resistance of these specimens is summarized in table 5. It was surprising that any of these passed the spall test, since magnesium appeared to make aluminum have poor spall resistance.

4. Spall resistance of silica-rich, alumina-rich, and magnesia-rich enamels.

Silica, alumina and magnesia were substituted respectively for the titania in the mill addition of the basic tan enamel. When these enamels were applied to prefired 3003, they showed excellent spall resistance except for the magnesium-rich enamel, which showed some small interior spalling.

5. Spall resistance of silica-free, lead-free and basic white lead-silicate enamels.

Spall test results on a special set of silica-free and lead-free enamels applied to 1199, 1199 with 2% Mg, 1199 with 1% Mg_2Si, and 6061 were compared with the spall test results for the basic white lead-silicate enamel applied to these same metals. These results are presented in table 6. It will be noted that all the silica-free enamels are listed as having spalled completely. Actually, these enamels were dissolved by the antimony trichloride test solution since there was no glassy residue remaining in the test solution.

6. Spall resistance of enamels fired with increasing amounts of water in the furnace atmosphere.

Water in amounts varying from 0 to 200 cc was added to the furnace atmosphere in which the standard enamel was fired on pickled 5086 and 6061. These specimens were then spall tested and sectioned. All the enameled 6061 specimens passed the spall test while all the enameled 5086 specimens failed. There was no marked difference in the cross-sections of each alloy as the amount of water added was increased.

3.1.2 Spall Testing Deformed Specimens

Industry members of the Aluminum Council reported that spall testing enameled specimens after deforming them over a mandrel gave a better correlation between laboratory spall resistance tests and field experience than spall tests on undeformed enameled specimens. Therefore, a mandrel with radii varying from 1/8 to 7 inches was designed and used in preparing a new set of specimens for spall testing. One half of the 3 x 9-inch specimens were deformed over the mandrel before testing and the other half were tested flat as control specimens. The spall test results on the deformed and flat specimens were similar (see table 7). 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.

3.1.3 Effect of Humidity on Spall Resistance of Specimens

The Aluminum Council members also reported cases of spalling after exposure to high humidity. The first investigation of spalling caused by humidity 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 alloy with 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 cycles. After six 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 slight additional spalling after the 6th cycle.

3. Total immersion in hot (170°F) distilled 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 test was run for four cycles with no spalling.

and one hour dry. This was run continuously for seven weeks with no spall failures occurring.

3.2 Analyses of Spall Test Solutions

Spent spall solutions for three spall test methods 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 specimens of 1100, 6061, and 5086 alloys 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 8 for a summary of these test results).

Quantitative analyses of the spent antimony trichloride spall solutions, after samples of prefired 1100, 6061, and 5086 had been tested showed that the solution in which the 1100 was tested contained 0.3 mg of magnesium, that from the 6061 contained 31 mg, and that from the 5086 contained 165 mg. The relative amounts of magnesium in the spall solutions correlated fairly well with the amount of spalling observed on the enameled samples. For that reason another quantitative analysis for magnesium and chromium (chromium is used in pickling and is thought to tie up the magnesium) 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 (without enamel) were tested. A summary of these results is presented in table 9. Although these results again indicated an increase in magnesium with increased spalling, determinations of the unenameled metal blanks indicated a similar increase. When the values for the blanks (either for 100 percent bare metal or corrected by multiplying by the percentage spalling which occurred on the specimens) 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.

3.3 Oxide Layer

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

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 companies measured the thickness of the oxide layer after removing it from the metal by dissolving 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 10.

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 11.

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 12. 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 (or magnesium oxide) was also taken into solution by the enamel.

3.4 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 the electron microscope and electron microprobe and to observe the microstructure of many enamel-metal systems.

The observations with the light microscope include studies of the effect of different pretreatments on Mg_2Si, Mg_5Al_8, αAlFeSi and $FeAl_3$ second phase constituents of these alloys. These studies indicated 1) the enamel by itself attacked only Mg_2Si, 2) the hot acid chromate deoxidizer plus enamel severely attacked the Mg_2Si and Mg_5Al_8 and slightly attacked the αAlFeSi and $FeAl_3$, 3) the hot acid chromate deoxidizer followed by the alkaline chromate and enameling attacked the Mg_2Si and Mg_5Al_8 about the same as the hot acid chromate and enameling but the αAlFeSi and $FeAl_3$ appeared to be protected from attack by the addition of alkaline chromate, and 4) alkaline chromate and enameling showed only slight attack on the Mg_2Si and Mg_5Al_8 and no attack on the αAlFeSi or $FeAl_3$.

A series of photomicrographs taken with polarized light showed an interesting difference 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 of vapor deposited chromium and enameled specimens (which did not spall) showed a black layer along approximately 50 and 20 percent, respectively, of the interface while 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.

Studies of prefired 5086, enameled and fired for ten hours corroborated the existence of a "reaction" zone (see figure 1). It was also found that the zone contained lead and Mg_2Si particles and a magnesium-rich (brown) zone. Evidently, it was this magnesium rich zone that we saw earlier as the black layer. When attempts were made to duplicate this result, it was found that the width of the reaction zone varied considerably. Therefore, attempts were made to determine the cause of these inconsistent results by examining the effects of furnace atmosphere on the reaction products. Optical examinations of cross sections of enamels on 1199 + 1% Mg_2Si fired in air, oxygen, nitrogen, argon, argon 65% + hydrogen 35%, nitrogen + 30 mm water vapor, nitrogen at .003 mm and flowing oxygen indicated that the furnace atmosphere had a very pronounced effect on the reactions that occurred between the enamel and the metal. The reactions varied from no visible effect for the enamels fired in air (see figure 2), nitrogen and argon, to a brown magnesium-rich layer at the interface for the enamels fired in oxygen, and to having globules of lead, Mg_2Si and islands of a magnesium-rich phase present near the interface for enamels fired in hydrogen, a vacuum nitrogen or an atmosphere containing water vapor. These phases were generally located with the light microscope and identified with the electron microprobe.

Similar studies of lead-free and silica-free enamels on 1199, 1199 + 1% Mg_2Si, and 1199 + 2% Mg indicated that no reaction products were formed on 1199 coated with either one of the enamels and fired in hydrogen, or coated with the silica-free enamel and fired in an argon atmosphere. Reaction products were not noted on any of the other specimens of 1199. Fine spherical particles of metallic cadmium were present throughout the lead-free enamel applied to both Mg_2Si- and Mg-containing alloys, except those fired in the oxygen atmosphere. These magnesium-containing alloys fired in oxygen had a non-continuous, magnesium-rich phase present adjacent to the interface. The silica-free enamels fired on all these alloys, in all atmospheres except oxygen, produced discreet particles of lead-boron phase. Again, these particles were located with the light microscope and identified with the electron microprobe.

3.5 Electron Microscopy

Replica electron microscopy has been used extensively to study the interfacial area on spalling and non-spalling enamel-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 from the enamel to the metal on the alloys that spalled (see figures 3 and 4). However, this difference was detected only after etching. Studies of the effects of many different etchants, including antimony trichloride, substantiated the above findings.

The amount of oxide solution (see Section 3.3) was monitored by replica electron microscopy methods.

Transmission electron microscopy was used on one set of enameled 6061 specimens. This set of micrographs showed a marked difference in the transition across the interface on the specimens that spalled and those that did not spall. The interface on the systems that did not spall appeared smooth from the metal to the enamel with a fairly wide intermediate zone; on the other hand, the systems that spalled showed a narrow band that appeared separated from the enamel.

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

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.

3.6 Electron Microprobe

The electron microprobe was used extensively (see tables 13 and 14) 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.

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 lead to further investigations to locate other elements that might be combining with the magnesium in the alloys where spalling did not occur.

The probe plots in figure 5 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. (6061 was the alloy used for these four samples). Also, the relative concentration of potassium at the interface was greater than the relative concentration of sodium for the systems that did not spall while the opposite was true for the systems that did spall.

A probe study of pure magnesium that had been prefired, pickled or anodized prior to enameling indicated that the potassium diffused further into the magnesium than the sodium on the systems that did not spall (anodized and pickled magnesium) while they diffused about equally into the magnesium on the system that did spall.

A probe study of pickled and prefired 1199 that had been fired for 10 hours indicated that lead migrated to the interface more readily than potassium on the prefired sample which spalled. The reverse was true for the pickled sample which did not spall.

There was no noticeable diffusion between constituents of the enamel and the metal when the individual probe traces were observed. However, this data indicated small differences in the width of the diffusion zone. The overplotted data illustrated in figure 6 indicates that there is a relatively wide diffusion zone between the porcelain enamel and the 1100. The diffusion zone for the 6061 is slightly narrower than for the 1100 and probably contains reaction products as indicated by the presence of lead and magnesium in the diffusion zone between the maximum concentrations of aluminum and silicon. The diffusion zone in the 5154 alloy apparently contains more reaction products as indicated by the increased concentration of lead and magnesium. 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 diffusion and reaction products in the diffusion zone affects the spall resistance of enamel-metal systems.

3.7 X-ray Powder Diffraction

After pickling, 6061 alloy specimens were coated with a clear lead-bearing enamel and fired for 10 minutes. The enamel was abraded to produce a series of specimens with decreasing thickness of enamel (approaching the interface). X-ray powder diffraction analyses of the remaining enamel revealed increasing amounts of metallic lead as the interface was approached. Additional studies revealed greater concentrations of lead near the interface when the enamel was applied to a magnesium bearing metal such as 5052 than with the magnesium-silicon alloys such as 6061 and 6063 and essentially no concentration of lead near the interface with the relatively pure alloys such as 1100.

3.8 PEI Adherence Tester

Prior to the initiation of this program, Laboratory G had evaluated the spall resistance of some enameled aluminum specimens by deforming them as described in ASTM C-313. These specimens were 3/8 inch thick extrusions with the enamel varied to change the spall resistance. The appearance of the deformed areas ranged from some fractures occurring within the glass for systems with good adherence to bright metal for systems with poor adherence. These results also correlated fairly well with the results of the antimony trichloride test on these specimens.

3.9 Direct-Tension Pulling Tests

A direct-tension pulling test was 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"; this is often referred to as a "button tester". The test consisted of epoxying a one-inch diameter button on the enamel surface and then pulling on the button until it was removed along with some enamel.

Preliminary tests on a set of enameled specimens indicated that the appearance of the "buttonhole" correlated better with spall resistance than did the force required to remove the button (see table 15). 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. The fractures for pickled 5086 and for both pickled and prefired 6061 were between these two extremes. The visual observations were supported by measurements of the conductive surface of the buttonholes as described in ASTM C-313. The 1199 has practically no conductive area while the prefired 5086 has the largest areas. However, the differences between these extremes are not consistent enough to be the basis of a new test.

These results indicate that, mechanically, the weakest area of the 1199-enamel system is well into the glass - perhaps at the edge of the relatively wide diffusion zone between the enamel and the alloy (see section 3.6). The weakest area in the 6061 systems appears closer to the alloy while the 5086 systems often fracture right at the enamel-metal interface. It is possible that as the magnesium content of the aluminum is increased, more reaction products are formed in the diffusion zone, making it mechanically weak.

The enamel and metal sides of the tensile fracture on both prefired and pickled 6061 were examined with the electron microprobe 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 in the diffusion zone on pickled and enameled 6061 than on prefired and enameled 6061. This study also indicated that the enamel-metal system is mechanically weakest on the enamel side of the diffusion zone.

4. THEORY FOR THE RETENTION OF ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

The data obtained to date suggest that good adherence and good resistance to spalling of porcelain enameled aluminum requires a diffusion of aluminum or aluminum oxide into the enamel. This diffusion is illustrated by electron microprobe results (section 3.6) and by partial or complete solution in the enamel of the original oxide layer on the aluminum (section 3.3). The resulting diffusion zone is not subject to chemical degradation (section 3.5) and is mechanically stronger than the enamel (section 3.9). Magnesium is either absent from the diffusion zone or is associated with enrichments of alkali metals, particularly potassium (section 3.6).

When spalling occurs, the diffusion zone contains a layer of reaction products. This diffusion zone may contain magnesium in some form, frequently in large concentrations, and there is no potassium enrichment associated with the magnesium (section 3.6). Lead and magnesium silicide have also been observed in the diffusion zone (sections 3.4 and 3.6). This diffusion zone is susceptible to chemical degradation (sections 3.4 and 3.5) and, in mechanical tests, (sections 3.8 and 3.9), it seems as though it either breaks itself or it breaks away from the metal surface. The formation of reaction products in the diffusion zone apparently inhibits the formation of a relatively wide, homogeneous diffusion zone that is necessary for good adherence. A simplified illustration of the diffusion zones for systems with good and poor adherence is given in figure 7.

Commercially pure aluminum generally has good adherence and a relatively wide diffusion zone without a concentration of reaction products. Aluminum-magnesium alloys with poor spall resistance show a reaction layer in the diffusion zone. When chromium, or its compounds, are present on the surface of the aluminum-magnesium alloys, spalling is usually diminished but not eliminated. It is assumed that chromium inhibits the accumulation of reaction products in the diffusion zone. However, the function and mechanisms 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 3.1) and the condition of its surface before enameling (section 3.1 and 3.4). Here again chromium plays an important role but it is not the only factor.

There appear to be interdependent mechanisms involved when spalling occurs. Apparently the spall solution attacks the aluminum, and possibly the reaction layer, producing a corrosion product and a gas. The corrosion product and gas appear to build up pressure under the enamel layer which causes the enamel to flake away from the metal. It could be that a crack is initiated when the spall solution attacks the aluminum at the interface and this crack propagates more readily in systems where reaction products are present to act as stress concentrators than in systems which do not contain reaction products.

5. ROUND-ROBIN TESTING OF 6063 ALLOYS

After the theory was suggested, it was decided to see whether the knowledge gained could be used to predict how to successfully enamel extruded 6063 alloy commercially. This study included four steps.

The first step was the enameling of nine lots of extruded 6101 alloy. This is a closely controlled alloy occurring within the broad range of 6063 compositions. These nine lots of 6101 were enameled by a commercial firm using their standard pretreatment, enamel and firing procedures. The enameled specimens all passed the antimony trichloride spall test. Electron microprobe and optical microscopy failed to show any differences at the interfacial areas of the specimens, thereby suggesting that differences in spall resistance were minor.

Since the results of the first step were encouraging, it was decided to proceed with a round-robin test of six 6063 alloys from 3 primary and 2 secondary suppliers. These specimens were enameled by 5 processors of architectural porcelain enamels on aluminum. From the results of spall tests on these specimens, it appeared that there must have been differences in the enamel-pretreatment-firing steps used by the processors to account for the difference in the spall resistances of the final products. This conclusion was reached when it was observed that one enameler was able to enamel all 6 lots of 6063 with no spall failures, while the others were only able to enamel 2 or 3 lots of the 6063 without spall failures (see data in table 16).

Since the second step illustrated that it was possible to successfully enamel 6 different lots of 6063, it was decided to control two of the processing variables in another round-robin test. In the third step, 4 of the 5 enamelers participating in step II again enameled the 6 lots of 6063. This time, each enameler applied the same enamel to the 6 lots of 6063 alloys. When these specimens were evaluated after spall 20 hours in the $SbCl_3$ test solution, it was found that the spall resistances of samples produced by 3 of the 4 manufacturers now passed the spall test (see table 16). In communications with the enamelers, it was found that the enameler whose samples failed the spall test was the only one who did not use a chrome-containing deoxidizer. Furthermore, of the 3, only one employed it at ambient temperature. In order to confirm the effects of the deoxidizer, the fourth step was initiated. In this step, duplicate specimens (12 different shapes, all 3-ft sections) of 4 lots of aluminum were pretreated in a hot acid-chrome-containing deoxidizer and an ambient temperature chrome-free deoxidizer. The same enamel was applied to both sets of specimens. They were fired and spall tested. After one cycle in the antimony trichloride spall test solution, only one lot of aluminum that had been pretreated with the ambient temperature, chrome-free deoxidizer failed the test. It was then decided to extend the spall test by three cycles. At the end of four 20-hour cycles, in the antimony trichloride spall test solution, gross failures were noted on one additional lot subjected to the ambient temperature, chrome-free deoxidizer while none of the hot-acid chrome treated specimens failed. It, therefore, seems that 6063 extursions can be porcelain enameled if care is taken in the selection of the enamel and the pretreatment used.

6. SUMMARY OF FINDINGS AND TECHNIQUES USED IN STUDYING THE MECHANISMS OF ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

A study of the mechanisms of adherence of porcelain enamel to aluminum has been undertaken during the past seven years. During this study, both commercially available and specially prepared aluminum alloys and enamels have been studied with light and electron microscopy, electron microprobe, and X-ray diffraction. They have been chemically tested in antimony trichloride and ammonium chloride spall test solutions, and mechanically tested by deforming and tensile testing. These studies have resulted in a theory for the adherence of porcelain enamel to aluminum which is that good adherence is the result of the diffusion of aluminum or aluminum oxide into the enamel without the formation of reaction products in the diffusion zone.

Several findings which relate to enamel-metal systems which spall easily, which do not spall, and findings which relate to all systems are given below:

Summary of findings relating to easily spalled systems

A. The interface is mechanically weak

   1. Enamel is readily removed by direct-tension pulling

   2. Enamel is readily removed by deforming

B. Etching solutions preferentially attack the interface of cross-section

   1. In major cases, this can be observed with the light microscope

   2. This can always be observed at high magnification with electron microscopes

C. Large concentrations of magnesium are sometimes found close to the enamel-metal-interface

D. The oxide layer is not reduced in thickness

E. The oxide layer is rich in magnesium

F. Flakes of enamel fracture off with force in spall solutions

G. Reaction products containing lead and magnesium are often found in the diffusion zone.

Summary of findings relating to non-spalling systems

A. The interface is strong

   1. Direct tension pulling tests fracture the system in the porcelain enamel

   2. Deformation tests fracture the system in the porcelain enamel

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

C. Magnesium concentrations at the interface are associated with concentrations of alkali metals or are non-existent

D. A relatively wide diffusion zone exists

E. The oxide layer is reduced in thickness

F. Potassium diffusion results in enrichments of potassium at or near the interface.

Summary of findings relating to all systems

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

B. Various humidity exposures, accelerated weathering tests, etc., have not produced accelerated spall failures which could be duplicated

C. Elements dissolved by the spall test solution reflect the composition of the alloy being tested rather than the composition of the enamel at the interface

D. Moisture in the furnace atmosphere does not affect the spall resistance of a given enamel-metal system.

7. ACKNOWLEDGMENT

This report would not be complete without acknowledging those companies that contributed to this project. The Ferro Corporation (the frit company) should be acknowledged for donating the full-time services of a research associate on this project for three and a half years, for preparing the enameled samples and providing additional technical guidance concerning the porcelain enamel composition and properties. The four aluminum companies participating in this project, the Aluminum Company of America, The Aluminum Company of Canada, The Reynold's Metals Company and the Kaiser Metal and Chemical Company, should also be acknowledged for contributing technical guidance regarding the metallurgy of aluminum and for performing many of the laboratory analyses reported herein. These five companies, together with the remaining member companies of the Aluminum Council, should also be acknowledged for their financial assistance which made this project possible.

8. BIBLIOGRAPHY OF PREVIOUS REPORTS OF THIS STUDY

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B. Unpublished Reports*

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6. Proceedings of the Porcelain Enamel Institute Technical Advisory Committee Seminar, Aluminum Council 1970.

*Although these are unpublished reports to the sponsor, they are available through the sponsor, the Porcelain Enamel Institute, 1900 L Street, N. W., Washington, D. C. 20036.

Table 1. Compositions of the Alloys Used[d/]

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
1199, 1% Mg_2Si	98.949	0.62	----	0.43	0.001	----	----	----	----	----	----	----
1199, 2% Mg	98.115	1.87	0.002	0.001	0.001	0.01	0.001	----	----	----	----	----
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[c/]	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	99.432	0.28	0.02	0.04	0.07	0.02	0.005	----	0.003	0.002	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	0.10	000	0.01	0.26	----	----	----	----
5086[c/]	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.

c/ Composition may vary slightly toward the end of the program as the initial, analysed lots of aluminum were replaced.

d/ The alloys 3003, 5053, and "high purity magnesium" were not analyzed for exact composition.

Table 2. Oxide Composition of the Basic Tan Enamel, Including Both the Frit and Mill Additions.

Oxide	Weight Percent
PbO	26.47
TiO_2	24.85
SiO_2	22.38
Na_2O	10.46
K_2O	3.67
BaO	3.22
Sb_2O_5	2.33
Li_2O	1.67
B_2O_3	1.41
Cr_2O_3	1.28
ZnO	0.99
Fe_2O_3	0.96
Al_2O_3	0.32

Table 3. Oxide Compositions of the Frits Used in the Lead-Free, Silica-Free and Basic White Lead-Silicate Enamels.

Oxide	Weight percent in frits for:		
	Basic White Lead-Silicate Enamel	Lead-Free Enamel	Silica-Free Enamel
PbO	33	0.05	high
TiO_2	14	18	high
SiO_2	30	30	0.05
Na_2O	12	18	low or absent
K_2O	2	10	n.d.
BaO	4	0.03	0.0
Sb_2O_5	3	2.8	0.0
Li_2O	2.0	3.5	0
B_2O_3	1.0	5	high
Cr_2O_3	0.0005	0.0005	0.00
ZnO	0.0	2	high
Fe_2O_3	0.1	0.05	0.05
Al_2O_3	0.2	0.5	0.05
MgO	--	--	0.05
P_2O_5	n.d.	2.5	n.d.
CaO	0.1	0.1	0.01
MnO_2	0.0003	0.0005	0.00
CuO	0.003	0.003	0.00
SrO	0.1	1.5	0.00
ZrO_2	0.0	0.05	present
Nb_2O_5	0.0	0.0	0.03
CdO_2	0.03	5	0.0
SnO_2	0.001	0.001	0.0

Table 4. 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
5154	Prefire	Fail
5154	Pickle	Fail
5257	Prefire	Pass

Table 5. Spall Resistance of Magnesium

Pretreatment	Spall Test Results
Prefire	Fail
Pickled	Pass
Vapor deposited chromium	Not Tested*
Anodized, unsealed	Not Tested**
Anodized plus vapor deposited chromium	Not Tested**
Anodized, water sealed	Not Tested**
Anodized plus sodium dichromate sealed	Pass

* 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 6. Summary of Spall Test Results on Lead-Free, Silica-Free, and Basic White Lead-Silicate Enamels

Pretreatment	Firing Time (min)	Spall Test Results[a] on Three Specimens of:											
		Lead-Free Enamels on:				Silica-Free Enamels on:				Basic White Lead-Silicate Enamels on:			
		6061	1199 1% Mg_2Si	1199 2% Mg	1199	6061	1199 1% Mg_2Si	1199 2% Mg	1199	6061	1199 1% Mg_2Si	1199 2% Mg	1199
Pickled	10	40% Spall	Pass	Pass	Pass	100% Spall	100% Spall	100% Spall	100% Spall	5% Spall	20% Spall	75% Spall	Pass
Prefired	10	30% Spall	Pass	Pass	5% Spall	100% Spall	100% Spall	100% Spall	100% Spall	30% Spall	10% Spall	20% Spall	Pass
Pickled	600	30% Spall	Pass	50% Spall	10% Spall	100% Spall	100% Spall	100% Spall	100% Spall	10% Spall	100% Spall	30% Spall	Pass
Prefired	600	30% Spall	Pass	20% Spall	5% Spall	100% Spall	100% Spall	100% Spall	100% Spall	80% Spall	99% Spall	20% Spall	25% Spall

a/ Those enamels listed as "spall" failed the test. The percentage given indicates the extent of the spalled area.

Table 7. 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	Deformed	Length of Spalled Area on Deformed Specimens (inches)
a) 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
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
b) 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 noticeable difference in spall resistance between the specimens. The rank was based on a visual estimate of the amount of bare metal exposed after spall testing.

Table 8. Summary of Qualitative Analys s of Spall Test Solutions

Element	Quantity in 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	0.51	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	x	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	--
Manganese	a	b	d	-	a	a	b	c	c	--	--	0.01	--
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				

* Percent concentrations of elements given in the table are as follows: a= <0.001, b= 0.001-0.01, c= 0.01-01, d= 0.01-1.0, e= 1.0-10.0, f= >10, - not detected and ? was barely detectable but definitely less than .001.

Table 9. Quantitative Analysis of Spall Test Solutions

Alloy	Enameled Specimens			Metal Blanks		Change in Concentration		Enameled Specimens			Metal Blanks		Change in Concentration	
	Total Mg (mg)	Total Cr (mg)	% Bare Metal (spall)	Total Mg (mg)	Total Cr (mg)	Mg (mg)	Cr (mg)	Total Mg (mg)	Total Cr (mg)	% Bare Metal (spall)	Total Mg (mg)	Total Cr (mg)	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	0.09	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 10. Oxide Thickness Measurements

Alloy	Mg Content	Thickness of Naturally Occurring Oxide Layer, Angstroms		Thickness of Prefired Oxide Layer, A Angstroms	
		Laboratory B	Laboratory C	Laboratory B	Laboratory C
1100	--	160	190	220	297
6061	0.85	236	393	620	840
6063	0.54	220	420	340	527
5657	0.79	110	233	400	577
5154	3.5	224	813	490	1310

Table 11. Magnesium in the Oxide Layers Occurring on Aluminum Alloys

Alloy	Mg Content	Magnesium in Naturally Occurring Oxide Layer, Percent		Magnesium in Prefired Oxide Layer, Percent		Difference in Magnesium Content of Naturally and Prefirèd 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	0.85	0.34	0.47	0.98	1.30	0.64	0.83
6063	0.54	0.00	0.06	0.51	0.83	0.51	0.77
5657	0.79	0.11	0.09	0.60	0.78	0.49	0.69
5154	3.5	0.37	0.78	1.34	1.64	0.97	0.86

Table 12. Summary of Oxide Solution Measurements on Anodized Aluminum and Magnesium

Specimen	Thickness of Anodized Layer Before Enameling Angstroms	After Enameling Angstroms	Change in Anodized Layer Angstroms
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)* 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 13. Elements Studied in Quantitative Electron Microprobe Analyses

Alloy	Pretreatment	Firing Time (min.)	Element												Lab
			Pb	Si	Mg	Al	Cu	Cr	Ti	Na	C	K	Fe	Mn	
1100	Chem. Clean	10	x	x	x	x									E
6061	Chem. Clean	10	x	x	x	x									E
5154	Chem. Clean	10	x	x	x	x									E
5154	Chem. Clean	10			x		x	x							E
6061	Chem. Clean	10			x		x	x							E
5657	Chem. Clean	10			x		x	x							E
1100		10	x			x									F
5154		10	x		x	x									F
5154		10			x										E
5154		10						x							C
6061		10			x			x							C
5154	Prefire	10			x	x				x					B
6061	Prefire	10			x	x				x					B
5086	Prefire	10			x										D
6061	Pickle	10			x										B
6061	Pickle	30			x										B
6061	Pickle	90			x										B
6061	Pickle	300			x										B
5086	Pickle	300			x						x				B
6061	Pickle	10			x							x			B
6061	Pickle	300			x					x		x			B
6061	Pickle	600			x					x					B
5086	Pickle	300			x					x		x			B
5086	Pickle	300			x					x		x			B

Table 13. (continued)

Alloy	Pretreatment	Firing Time (min.)	Element													Lab
			Pb	Si	Mg	Al	Cu	Cr	Ti	Na	C	K	Fe	Mn	Ba	
6061	Pickle	90			x											D
H.P. Mg	Prefired	10		x	x			x		x	x	x				A A
H.P. Mg	Pickled	10		x	x			x		x	x	x				A
H.P. Mg	Anodized, Dichromate Sealed	10		x	x			x		x	x	x				
6061	Pickled	10			x			x		x		x				D
6061	Prefired	10			x			x		x		x				D
6061	Pickled	600			x			x		x		x				D
6061	Prefired	600			x			x		x		x				D
6061	Pickled	10 (940°)		x	x			x		x		x	x	x		D
6061	Prefired	10 (940°)		x	x											
1199	Prefired	10	x	x	x	x		x		x		x				D
1199	Prefired	600	x	x	x	x				x		x				D
1199	Pickled	600	x	x	x	x	x	x	x	x		x			x	D
5086	Prefired	600	x		x	x				x						D

Table 14. Elements Studied in Quantative Electron Microprobe Analyses

Alloy	Pretreatment	Firing Time (min.)	Element												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	x	x	B
5154	Prefire	10	x	x	x	xx	x	x	x	x	x	x	x	x	x	B
5086	Prefire	600	x		x							x				D
5086	Pickle	600			x							x				D
6061	Pickle	600	x													D
6061	Pickle	600	x													D
5086	Pickle	10	x		x				x							D
5086	Pickle	30	x		x				x							D
5086	Pickle	90	x		x				x							D
5086	Pickle	300	x		x				x							D
5086	Prefire	10	x		x				x							D
5086	Prefire	30	x		x				x							D
5086	Prefire	90	x		x				x							D
5086	Prefire	300	x		x				x							D
6061	Pickle	10	x		x				x							D
6061	Pickle	30	x		x				x							D
6061	Pickle	90	x		x				x							D
6061	Pickle	300	x		x				x							D
6061	Pickle	10	x							x						B
6061	Pickle	30	x							x						B
6061	Pickle	90	x							x						B
6061	Pickle	300	x							x						B
5086	Pickle	10	x							x						B
5086	Pickle	30	x							x						B
5086	Pickle	90	x							x						B
5086	Pickle	300	x							x						B

Table 14. (continued)

Alloy	Pretreatment	Firing Time (min.)	Element													Lab
			Mg	Na	Al	Cu	Zn	Pb	Ti	Cr	Fe	Si	O	S	K	
5086	Prefire	10	x													B
5086	Prefire	30	x	x											x	B
5086	Prefire	90	x												x	B
5086	Prefire	300	x	x												B
6061	Pickle	10	x													D
6061	Pickle	90	x													D
6061	Prefire	10	x													D
6061	Prefire	90	x													D
6061	Prefire, Deoxidized Prefire	10	x													D
6061	Prefire, Deoxidized Prefire	90	x													D
6061	Prefire	10 (940°)	x									x				D
6061	Pickle	10 (940°)								x						D
6061	Prefire	10	x													D
6061	Prefire	600	x													D
6061	Pickle	600	x													D
6061	Prefire	10 (940°)	x													B
6061	Pickle	10 (940°)	x													B
6061	Prefire	10	x													B
6061	Pickle	10	x													B
6061	Prefire	600	x													B
6061	Pickle	600	x													B
6061	Prefire	10			x			x	x					x	x	E
6061	Pickle	10						x								E
5086	Prefire	600	x													D

Table 15. Summary of Direct Tension Pulling Test Results

Pretreatment	Firing Time (min.)	Firing Temp (°F)	Force Required to Pull Button (pounds per square inch)			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

Table 16. Spall Test Results from the First and Second Round-Robin Tests on 6063 Aluminum Alloys

Alloy No.	First Round-Robin				Second Round-Robin			
	Enameler				Enameler			
	A	C	D	E	A	C	D	E
3	Pass	Pass	Fail	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Fail	Pass	Pass	Pass	Pass	Pass
	Pass	Fail	Fail	Pass	Pass	Fail	Pass	Pass
5	Pass	Fail	Fail	Pass	Pass	Pass	Pass	Pass
	Pass	Fail	Fail	Pass	Pass	Pass	Pass	Pass
	Pass	Fail	Fail	Fail	Pass	Pass	Pass	Pass
6	Pass	Fail	Pass	Pass	Pass	Fail	Pass	Pass
	Pass	Fail	Pass	Fail				
	Pass	Fail	Fail	Fail				
7	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Pass	Fail	Pass	Fail	Pass	Pass	Pass	Pass
8	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
9	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Pass
	Pass	Pass	Fail	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Fail	Pass	Pass	Pass	Pass	Pass

Normal enamel structure showing glass grains and TiO_2 precipitate

Reaction Zone - Pb particles
Mg_2Si particles
Mg rich zone

Mg Depleted Zone, Mg - 1.6%, No Mg_2Si

Grey Al-Fe(Mn)Si phase

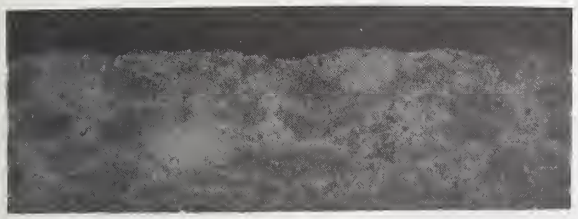
Normal 5086 Structure

Mg - 3.0%
Mg_2Si particles (Not distinguishable
Al-Fe(Mn)Si phase in black and white photograph.)
Al - aluminum matrix

500X

FIGURE 1

METALLOGRAPHIC CROSS SECTION OF ENAMELED AND SIXTEEN HOUR FIRED 5086 ALLOY SHOWING REACTION ZONE



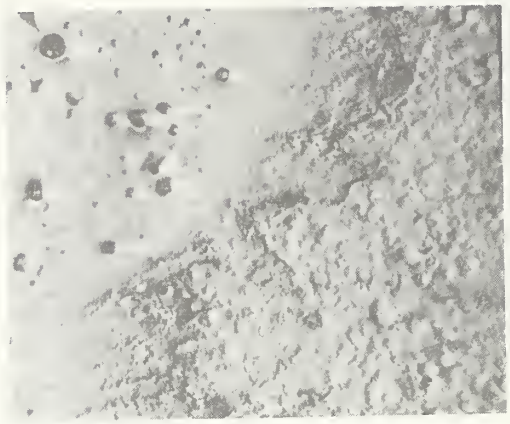
Normal enamel structure showing glass grains and TiO_2 precipitate

Normal 1199 + 1% Mg_2Si structure

FIGURE 2

METALLOGRAPHIC CROSS SECTION OF ENAMELED AND FIFTEEN HOUR FIRED SUPER PURITY ALUMINUM WITH 1% Mg_2SI. ILLUSTRATING THE ABSENCE OF ANY REACTION PRODUCTS. (500X)

Metal

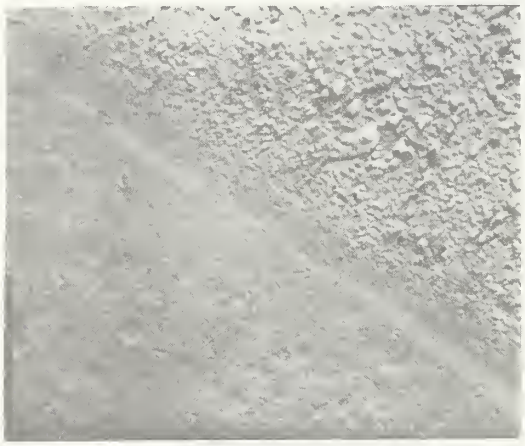


Enamel

FIGURE 3

PHOTOMICROGRAPH OF REPLICA OF POLISHED CROSS SECTION OF ENAMELED 1100 (GOOD ADHERENCE) ETCHED WITH 5% NaOH (8000 MAGNIFICATION)

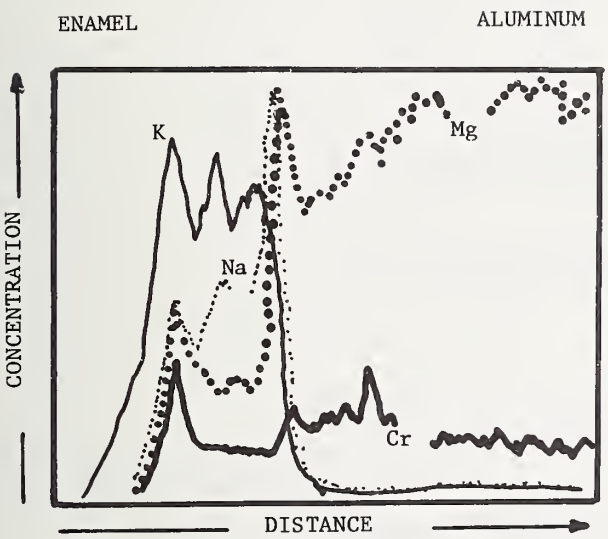
Metal



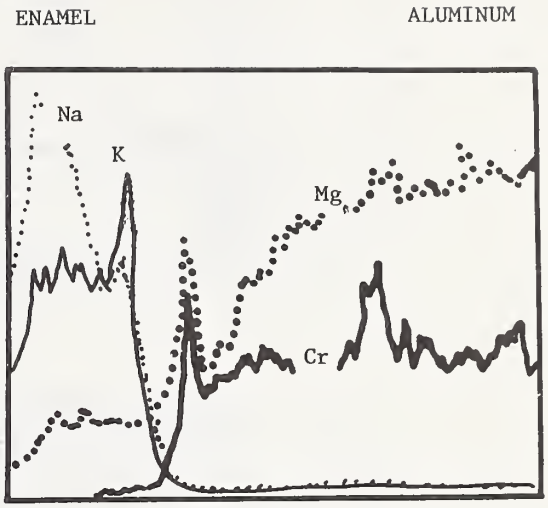
Enamel

FIGURE 4

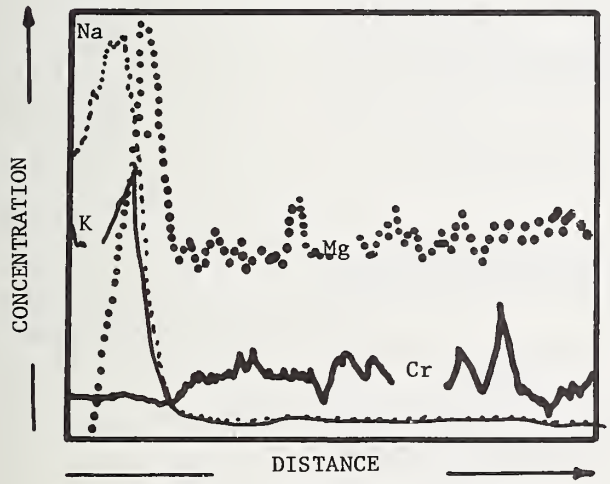
PHOTOMICROGRAPH OF REPLICA OF POLISHED CROSS SECTION OF ENAMELED 5154 (POOR ADHERENCE) ETCHED WITH 5% NaOH (8000 MAGNIFICATION)



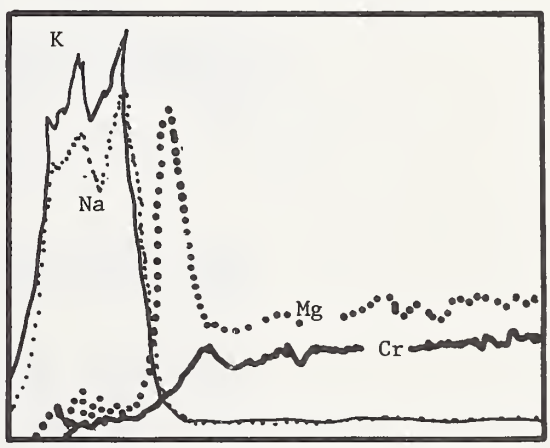
Prefired 6061, 10 min. at 1000°, Borderline Spall.



Pickled 6061, 10 min. at 1000°, No Spall.

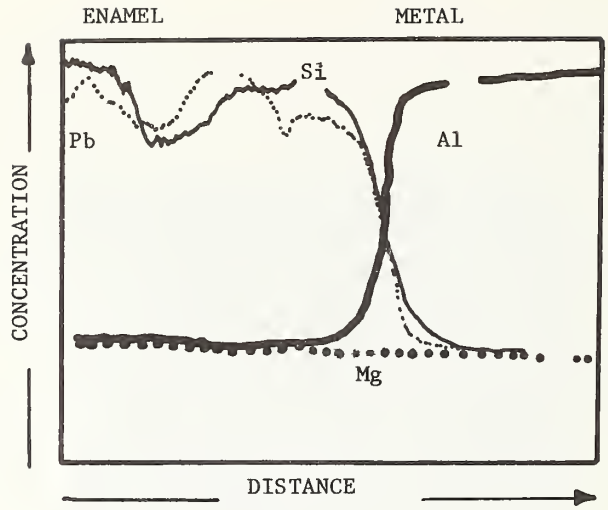


Prefired 6061, 10 hr. at 1000°, Spalled.

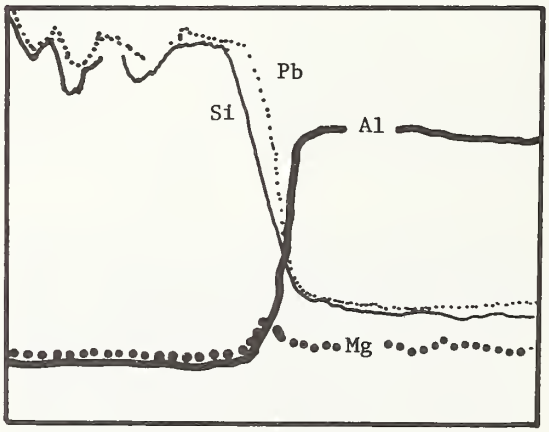


Pickled 6061, 10 hr. at 1000°, No Spall.

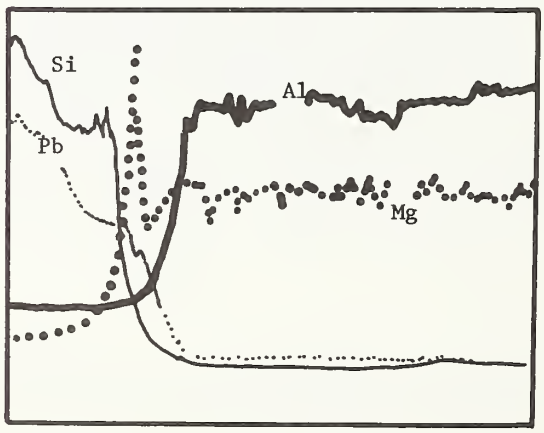
Figure 5. Microprobe traces for Sodium, Potassium, Magnesium and Chromium on 6061 with various pretreatments and firing condition.



Chemically Cleaned 1100, No Spalling.



Chemically Cleaned 6061, Borderline Spall.



Prefired 5154, Spalled.

Figure 6. Microprobe Traces for Silicon, Lead, Aluminum and Magnesium on 1100, 6061, and 5154.

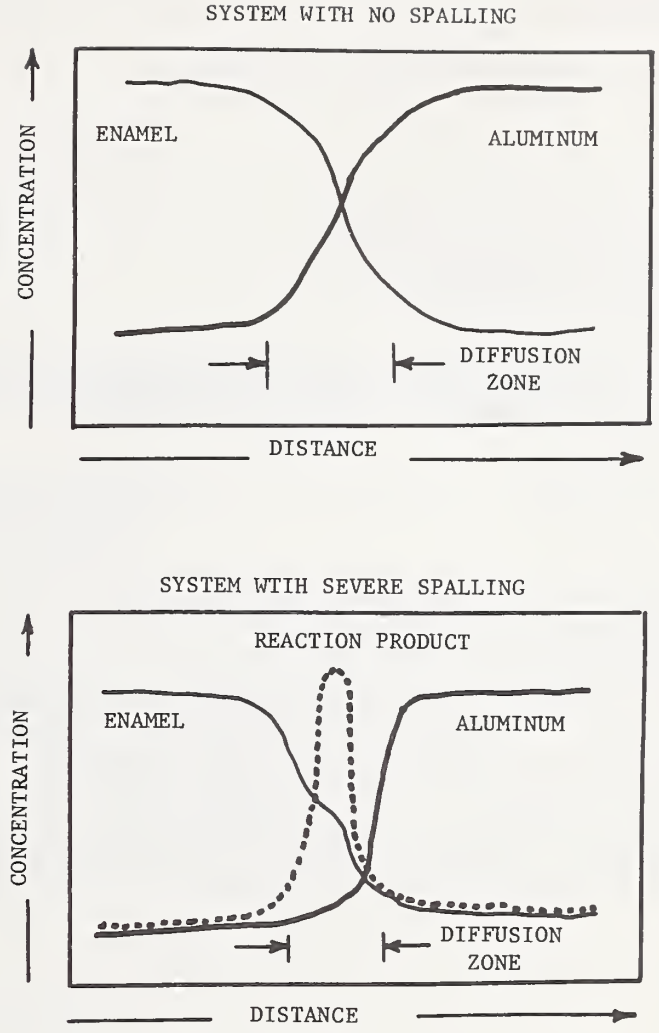


Figure 7. Schematic drawing of microprobe traces showing the concentration of a reaction product in the diffusion zone.

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Light and electron microscopy, electron microprobe, and X-ray diffraction techniques were used to determine the mechanisms of adherence of porcelain enamel to aluminum. A theory is presented that adherence depends upon diffusion of aluminum into the enamel and further, the diffusion zone should be relatively free of reaction products for the enamel-metal system to retain good adherence after exposure to chemical solutions or to weathering. Round-robin testing of 6063 aluminum alloy extrusions indicated that this alloy can be enameled if care is exercised in the selection of the enamel and the pretreatment.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Adherence; aluminum; electron microprobe; electron microscope; porcelain enamel; spalling; X-ray diffraction.

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