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# NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

May 1, 1967 through July 31, 1968

THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM



U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

## NATIONAL BUREAU OF STANDARDS

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## NBS PROJECT

421.04-12-4212270

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May 1, 1967 through July 31, 1968

## THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

by

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Sponsored by  
Ferro Corp.

Porcelain Enamel Institute Research Associateship

National Bureau of Standards

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## I. INTRODUCTION

The Research Associateship Program of The Porcelain Enameled Aluminum Council of the Porcelain Enamel Institute has now entered its third year. This program, being carried out at The National Bureau of Standards, has had as its objective a study of the mechanisms of adherence of porcelain enamel to aluminum. It is believed that poor adherence and the problem of spalling of the porcelain enamel from aluminum are related. Spalling, which involves the flaking or chipping off of the porcelain enamel from the aluminum, especially after exposure to weathering, is a problem with certain alloys of aluminum. For this reason, only commercially pure aluminum alloys and several other selected alloys may be enameled. Insight into the mechanisms of adherence, or into causes for spall failure, should lead to the ability to solve the problem of spalling or lead to the ability to accurately predict its occurrence by testing prior to the placement of enameled aluminum into service.

The summary of this report compiles the basic findings of the program to date. A more complete discussion of the methods and results follows this summary. Reference may be made also to NBS report number 9533 which bears the same title and which covers the period of August 1, 1966 to April 30, 1967.

## II. SUMMARY

Magnesium is an important key to the overall problem. Its presence can directly lead to spalling. Alloys containing magnesium, if enamelable, require rather extensive pretreatment before enameling.

Electron microprobe data indicate that magnesium concentrates at the interface, presumably at the outer surface of the oxide layer, as shown by much higher percentages of magnesium at the interface area than in the remainder of the alloy. This concentration occurs when the metal is heated above 350 degrees C (660°F)<sup>1,2,3</sup> and is accentuated on those systems which show spalling after enameling. The effect of this type of concentration, and the effect of magnesium in general is demonstrated when magnesium is vapor deposited on the surface of commercially pure aluminum alloys. Vapor-deposited Mg causes these normally enamelable alloys to exhibit spalling unless they are pretreated before enameling in the same manner as the magnesium bearing alloys.

Magnesium affects the general overall character of the oxide layer. Alloys containing magnesium normally form thicker oxide layers. The magnesium present in the oxide layer also apparently affects the reaction of the layer during enameling. On pure aluminum, the oxide layer is reduced in thickness during the

enameling process, but this is not the case with the oxide layer on the magnesium bearing alloys which have not had the layer altered by pickling. (We have no information on what happens to the thickness of the oxide layer during enameling on pickled aluminum.)

The spall test solutions, and notably the antimony trichloride test solution, rapidly attack the interface area of enameled Mg bearing alloys. It appears that the form of the magnesium in the interface area is especially soluble and vulnerable to attack, which could be a major reason for spall failure in light of the previously enumerated effects of magnesium. This remains, however, to be demonstrated conclusively.

Chromium as a pretreatment also has a marked effect upon the spalling characteristics of porcelain enameled aluminum. It eliminates or substantially reduces spalling on magnesium bearing alloys. On some alloys of low magnesium content, 6061 being a prime example, the proper application of chromium can completely eliminate spalling. On alloys with higher magnesium content, the spalling is greatly reduced. The form in which the chromium is applied does not seem to be a factor. The easiest way to accomplish the deposition is from an alkaline-chromate bath, but vacuum, vapor deposited pure chromium works equally well. There are indications that other metals,

such as copper and iron, when deposited on the surface are of benefit also, although to a lesser degree than chromium.

An oxide layer of some composition is always present on all aluminum alloys, even after pretreatment. It is not known exactly what happens to this layer when the wet, alkaline porcelain enamel slip is sprayed onto the aluminum, or exactly what happens during the firing process. However, as stated previously, it is known that certain amounts of pure aluminum oxide can be taken into solution by the porcelain enamel, and the presence of other metals, or their oxides, such as magnesium, chromium, copper and iron have various effects on this solution. Contrary to what was previously believed, however, complete solution of this oxide layer is not necessary to develop spall resistance. Instances have been noted where some of the layer remained after firing and yet these samples showed excellent spall resistance.

Finally, the feeling is that elements in the alloys other than magnesium, and possibly copper, have only a minor effect, if any, on the spalling characteristics of porcelain enameled aluminum. More specific work is planned in this area, however.

### III PROCEDURES AND DISCUSSION

#### A - ELECTRON MICROPROBE

Initially, electron microprobe data had pointed to the fact that magnesium concentrated in the interface area. Results also indicated that the magnesium peaks, on alloys which had been prefired only before enameling, were larger than the peaks on the same alloys which had been subjected to an R-100<sup>4</sup> pretreatment before enameling. In some cases, however, the results were erratic. Samples which were repeated did not always show the magnesium peaks.

In order to get a more positive feel for what the electron microprobe could show and to gain more confidence in the results, it was decided to run more microprobe tests. For this purpose, 90 degree cross sections of preheated and enameled 6061 and 5154 alloys were mounted in epoxy, ground and polished, with the final polish being gamma alumina on a felt polishing wheel. Microprobe scans were run on these samples by Aluminium Laboratories, Ltd., Kaiser Aluminum and Chemical Corp., and Reynolds Metals Co. Both line scans and area scans were represented in the final reports, and all showed increased concentrations of magnesium in the interface area to substantiate the previous results. There was some indication that the concentration was more continuous across the interface of 6061 than on 5154, but rather decided increases of magnitude of magnesium

concentration were noted at the interface for both alloys. Of interest also, were indications of sodium enrichment near the interface as reported by Kaiser, and a possibility of aluminum diffusion into the porcelain enamel as reported by Reynolds.

#### B - ANALYSIS OF SPALL TEST SOLUTIONS

Several attempts were made to study the reactions at the interface during the spall testing cycle. The analysis of spall test solutions before and after spall testing was one approach.

Initially, samples of 1100, 6061 and 5086 alloys, prefired and enameled on both sides, were spall tested in each of three solutions -- distilled water, 1% antimony trichloride and 5% ammonium chloride -- for 24 hours. Ten, 3" X 4" samples of each enameled alloy were exposed, one at a time, in each solution, with a ratio of one gallon of test solution per square foot of enameled surface area. The enameled samples were scored diagonally on both sides, through to the bare metal, prior to immersion in the test solutions. A qualitative, spectrographic analysis was run on the nine enameled metal-solution combinations plus the antimony trichloride and ammonium chloride stock solutions. Comparing the amount of spalling that took place in each enameled metal-test solution combination with the qualitative analysis indicated a trend toward higher magnesium content in those combinations which yielded the most spalling.

A more specific test was run following this. Again, preheated and enameled 1100, 6061 and 5086 were tested. For this test, only the 1%  $\text{SbCl}_3$  solution was used. All ten, 3" X 4" specimens of each prefired and enameled alloy were exposed simultaneously for the standard test time of 20 hours. After the spall testing, the solutions were checked by atomic absorption spectrometry for total magnesium content. The solution in which the enameled 5086 had been run yielded five times the amount of total magnesium of the solution in which the 6061 had been run. The 5086 spalled almost completely, while the 6061 showed a small to moderate amount of spalling.

#### C - SLOW MOTION PHOTOGRAPHY

A second approach to studying the reactions at the interface during spalling was to observe and photograph the interface by slow motion photography while the spall test was in progress. Preheated and enameled 5154 was placed in a 1% solution of  $\text{SbCl}_3$  and was photographed at approximately 10X with a slow motion camera attached to a microscope. A relatively vigorous reaction started almost immediately, with the formation of reaction products of several types. A black precipitate formed on the bare aluminum, with the formation being much faster and heavier at the interface. It was assumed that this precipitate was antimony which had been reduced from the solution

by the aluminum. Gassing and bubbling was much in evidence. The gassing concentrated at the interface and the bubbles appeared to originate from between the enamel and the metal as the corrosion proceeded inward along the interface. Also originating at the original interface and later oozing out from between the metal and the enamel were large amounts of a white gelatinous material. One theory of the cause of spalling is that the magnesium present at the interface is in a highly soluble or reactive state. This material is attacked by water and atmospheric salts, with the attendant evolution of gases and precipitates between the enamel and the metal prying or forcing the enamel from the metal. The slow-motion film appeared to substantiate this theory. The white gelatinous material could well have been a magnesium hydrate.  $MgO$  hydrates readily, with a volume increase in the neighborhood of approximately 20 to 1.

#### D - ELECTRON MICROSCOPY

The original results obtained by examining the interface with the electron microscope showed a good deal of promise, and much time has since been devoted to this approach.

Samples to be examined were mounted as 5 degree taper sections, with the porcelain enamel being on the underside of the taper wedge. The sections were rough ground on silicon carbide papers and polished

with first alpha aluminum oxide and the gamma aluminum oxide.

Various samples were run, with the alloys and metal pretreatment both being varied in order to explore the range of spalling susceptibility.

It was found that etching the samples after polishing was necessary in order to bring out microstructural differences in the materials. The type of etch used was found to be important also, and had to be changed for certain combinations in order to obtain the maximum amount of information. The first etch that was used was a solution of 5% (by weight) of NaOH for ten to fifteen seconds at room temperature. This showed some interesting general differences between spalling and non-spalling samples. The use of Keller's etch, in various strengths, alone and in combination with 1%  $\text{SbCl}_3$  was also quite informative.

In comparing the results of the various alloy-metal pretreatment combinations (the frit and mill addition has thus far in the program been kept constant) under various etching conditions, some trends were noted. Those specimens which showed spall, quite often show an intermediate layer at the interface, between the porcelain enamel and the aluminum. The more severe the spalling, the more continuous and/or thick this layer tends to be. Samples which do not spall, do not show the layer, (if the pretreatment method is something other than anodizing, which will be discussed in more detail later in this report.)

Fig. 1 is a good example of the type of interface the non-spalling specimens exhibit. Fig. 2 also shows the interface of a non-spalling sample. Due to a large relief step, resulting from a more severe etch, adequate shadowing was not achieved in the immediate interface area on this micrograph, which makes interpretation difficult. It does point out however, the necessity of changing etches to fit particular samples.

Figs. 3, 4 and 5 illustrate the interface of a specimen showing moderate spall failure. They illustrate the interface layer and its variation in continuity.

Fig. 6 shows a severely spalling system. Taking into account the higher magnification used here, the interface layer is even thicker in this system.

Using 1%  $\text{SbCl}_3$  as the etchant, either alone or in combination with another etch, indicates that the specimens exhibiting spalling are more readily attached than those which do not exhibit spalling. The more severe the spalling, the wider and deeper is the area at the interface attacked by the  $\text{SbCl}_3$ . Figs. 7 and 8 illustrate that although  $\text{SbCl}_3$  will attack aluminum, (Fig. 7) it does not seem to preferentially attack the interface. In Fig. 8 the interface (where the metal and the porcelain enamel actually join) is still largely intact, even though there has been quite a bit of the metal attacked

and removed below the interface area. Figs. 9 and 10 also show the interface of a sample which exhibited spalling. The attack by the  $\text{SbCl}_3$  is especially severe in Fig. 9, having etched the interface deeply. Fig. 11 shows the same system illustrated in Figs. 9 and 10. The sample in Fig. 11 had a less severe  $\text{SbCl}_3$  etch, and the resultant attack is very small. As a further note, although examples are not shown, specimens of preheated and enameled 5154 which normally exhibit almost complete spalling, show such a severe attack when etched with the  $\text{SbCl}_3$  that the area of attack cannot be included in a single micrograph, even at relatively low magnifications such as 1000X.

Another interesting use of the electron microscope is in the taking of three dimensional micrographs. Figures 12 through 15 are examples of this technique. (A hand stereo viewer should be used as an aid in viewing these micrographs.) Any relief due to etching, etc. is dramatically shown by this method. Note particularly Figures 14 and 15. Fig. 14 gives some indication of the rather rapid and deep attack of the interface by  $\text{SbCl}_3$ . Fig. 15, a stereo view of Fig. 6, illustrates how stereo can help in interpretation. The layer separating the porcelain enamel and the aluminum is brought into sharper view, and the difference in its etch rate is shown as being faster than either the enamel or the metal as evidenced by its differing elevation.

In another phase of electron microscopy, Kaiser and Dr. A. L. Friedberg, Professor and Head of the Dept. of Cer. Engr. of the University of Illinois, have done some preliminary work on examining enameled specimens with scanning electron microscopes. It is hoped that some information and photographs from this work will be available for discussion in the next report.

#### E - LIGHT MICROSCOPY

Light microscopy was also used to examine the interfaces after etching tapered sections with spall solutions. This work was performed both at the Aluminum Company of America and at NBS. Alcoa examined preheated and enameled 6061, pickled and enameled 6061, preheated and enameled 5154 and preheated and enameled 1100. The examinations were made in both the "as polished" condition and after exposing the sections for various periods of time to an  $\text{NH}_4\text{Cl}$  etch. Little difference can be seen between the samples in the "as polished" state, but the  $\text{NH}_4\text{Cl}$  etch shows some noteworthy differences. Relatively short exposure times (measured in minutes) are needed on the preheated 6061 and 5154 to show considerable attack in the interface area at 100X mag. On the pickled 6061, 12-1/2 hours were needed to show any degree of etch. The prefired 1100 sample, viewed at 500X, showed some attack after 12 hours. This attack appeared to be very localized, and as was shown by electron microscopy in Figs. 7

and 8, the attack did not completely destroy the interface as it is prone to do on 6061 and 5154.

The light microscopy of a corresponding nature performed at NBS gave similar results. This again points to the extremely important role of chromium in altering the interface chemistry and helping to protect the system against spalling.

#### F - MAGNESIUM SILICIDE

During the period of this report, a limited amount of work was done on the size of  $Mg_2Si$  versus susceptibility to spalling. Specially heat treated 6063 alloy was supplied for this work by Aluminium Laboratories, Ltd. This aluminum had been treated in four different ways so that the magnesium silicide would be in solid solution in one sample, submicroscopically precipitated in another sample, coarsely precipitated in a third sample and very coarsely precipitated in the fourth lot. These variations were pickled and enameled, and the resulting enameled samples were checked for spalling. The results indicated that the physical manner in which the magnesium silicide is present in the aluminum may be very important. Having the magnesium silicide either in solid solution or in the form of a coarse precipitate appeared to be detrimental to good spall resistance. Conversely, the indications were that if the magnesium silicide were very finely or very coarsely precipitated,

better results could be expected. This might be important in light of how small additions of alloying constituents can affect the crystalline size of other constituents.

#### G - SOLUTION OF OXIDE LAYERS

Finally, work was done with anodic layers to determine, if possible, the solubility level of the oxide layers into the porcelain enamel. In the initial experiment, 99.99% purity aluminum (1199) was anodized. Portions of this material were cross-sectioned and the anodic layer was measured using the electron microscope. The remainder was porcelain enameled, and an attempt was made to measure the amount, if any, of the oxide layer dissolved by the enamel. Before enameling, the oxide layer measured approximately 6,000 angstroms in thickness. After enameling, the layer was not detected, indicating that at least this amount can be absorbed by the porcelain enamel.

A second experiment performed in the same way examined 1199 and 5053 (an alloy containing magnesium), each with nominal anodic layer thicknesses of 0.01, 0.1 and 1.0 mils. Before enameling, measurements of the anodic layer on the 1.0 mil (nominal) samples gave results of 210,000 A° (1.0 mil = 254,000 A°) for 1199 and 221,000 A° for 5053. At this thickness of anodic layer, the stress in the system was apparently so great that spontaneous spalling of the enamel

occurred on both alloys during cooling. At the 0.1 mil (nominal) thickness, the anodic layer on 1199 measured 26,000 A° and 20,000 A° on 5053. After enameling, the layer measured 21,000 A° on 1199, again indicating solution of some aluminum oxide into the porcelain enamel. However, this sample did not spall when tested in the 1% SbCl<sub>3</sub> spall test. This would indicate that a layer of undissolved oxide at the interface is, in itself, not necessarily a condition conducive to spalling. The composition, physical form and/or reactivity of this layer with moisture, etc. is probably more important in spalling than its presence. After enameling the 0.1 mil (nominal) 5053, the anodic layer measured 22,000 A° thick. This represents a slight increase in thickness after firing. Either the layer grows slightly during the firing process and the porcelain enamel does not take any oxide into solution, or the layer is growing faster than the porcelain enamel is taking it into solution. It should also be noted that this 5053 sample failed the SbCl<sub>3</sub> spall test. The measurements of 0.01 mil samples showed 3,000 A° before enameling on 1199 and no layer visible after enameling, with good spall resistance. The 5053 samples measured 2,000 A° before enameling and 3,000 A° after enameling. In this case the 5053 did not spall in SbCl<sub>3</sub> after enameling.

#### IV CONTINUING WORK

One of the ultimate objectives of this program is to develop a "surefire" test for spall resistance that will enable the porcelain enameler to be confident that spalling will not occur in the future on his product. Ideally, this should be a relatively rapid test that can be easily run with a minimum of sophisticated equipment and trouble. A second objective would be the knowledge and ability necessary to expand porcelain enameling of aluminum to alloys not currently considered enamelable. This latter might be accomplished either by improved metal pretreatment methods or through improved aluminum metallurgical techniques. Our continuing effort combined with what we already know must therefore be pointed toward these two objectives. Thus, the work currently in progress involves:

- A. Continuing examination of the interface by electron microscopy, using reverse angle taper sections (taper sections with the porcelain enamel on the top of the wedge). Perhaps this will tell us more about the mechanics of attack at the interface.
- B. Further quantitative tests on used spall test solutions. This we hope will determine if the spall solution attack is on the metal or the oxide layer.

- C. Electron microprobe analysis of spalled enamel chips, metal exposed by spalling and non-spalled areas of spalled samples. This may help to determine the location and action of the magnesium present in the interface area.
- D. Electron microprobe analysis of samples enameled with chromium free enamel. This is a further attempt at developing a key to the method by which chromium acts beneficially.
- E. Determining the effect of other alloying constituents on spalling by vapor depositing thin films of Cu, Zn, Mn and Cr alone and in combination with Mg on pure aluminum.

With a better insight hopefully to be gained from the above outlined areas of work, it is anticipated that progress toward the goals of the program will continue.



## References

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2. W. W. Smeltzer, J. Electrochem. Soc., 1958, 105, 67
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4. R-100 Chemical Pretreatment Pat. #2,719,796 (Aluminum Co. of America). A chromic acid-sulfuric acid bath used to deoxidize or desmut the aluminum alloy surface.



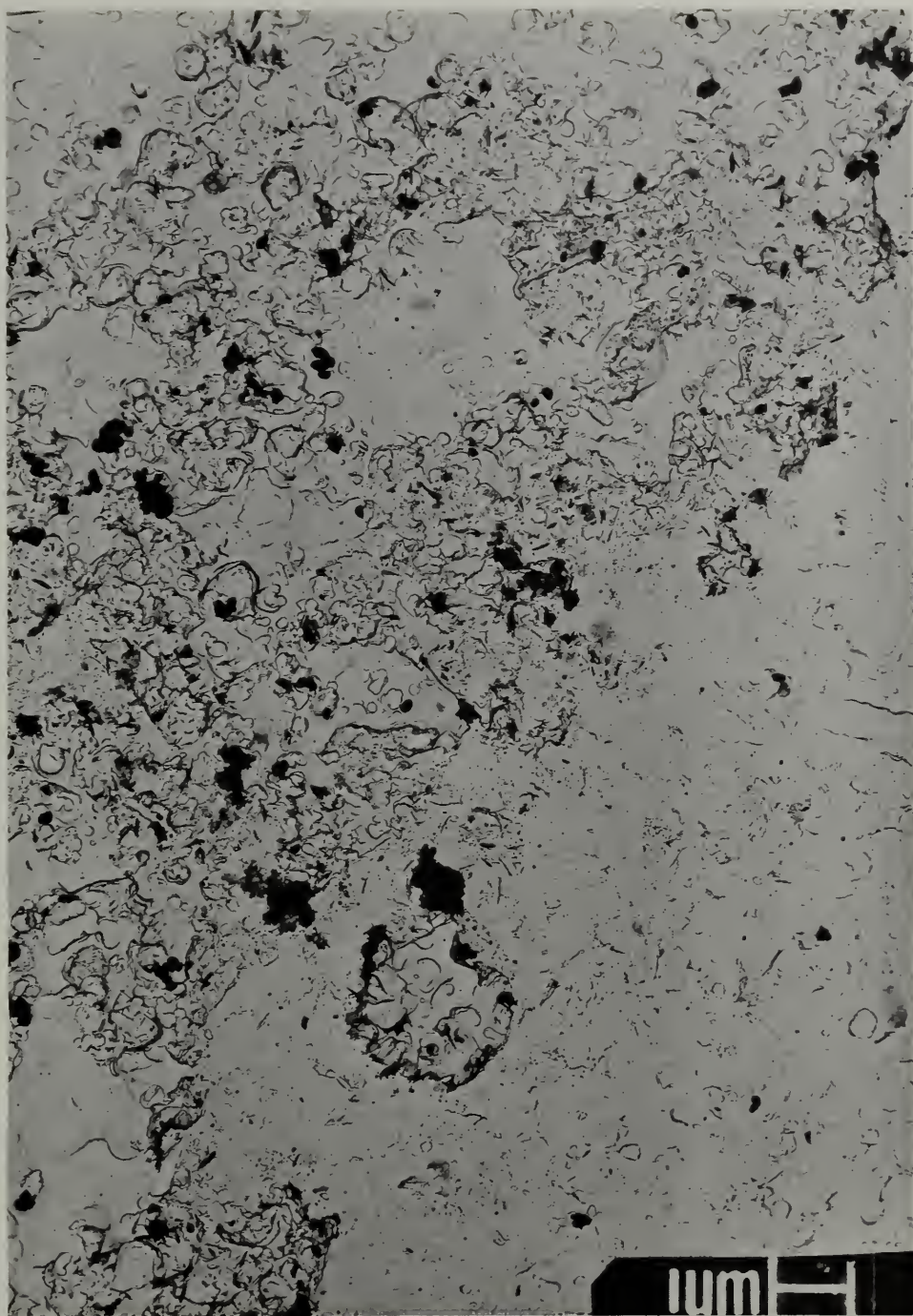


Fig. 1 6,900X. This replica was taken from pickled 6061 with good spall resistance. The specimen was etched with a 4:1 dilution of Keller's Etch for 10 sec. Compare this micrograph with Figs. 3 - 6.



Fig. 2 6,900X. 6061 pickled with resulting good spall resistance. Keller's Etch was given in two 15 sec. exposures, each exposure followed by a very light buff on a felt polishing wheel.

The glass is preferentially attacked, resulting in a large step as shown by the area of light shadowing adjacent to the interface.

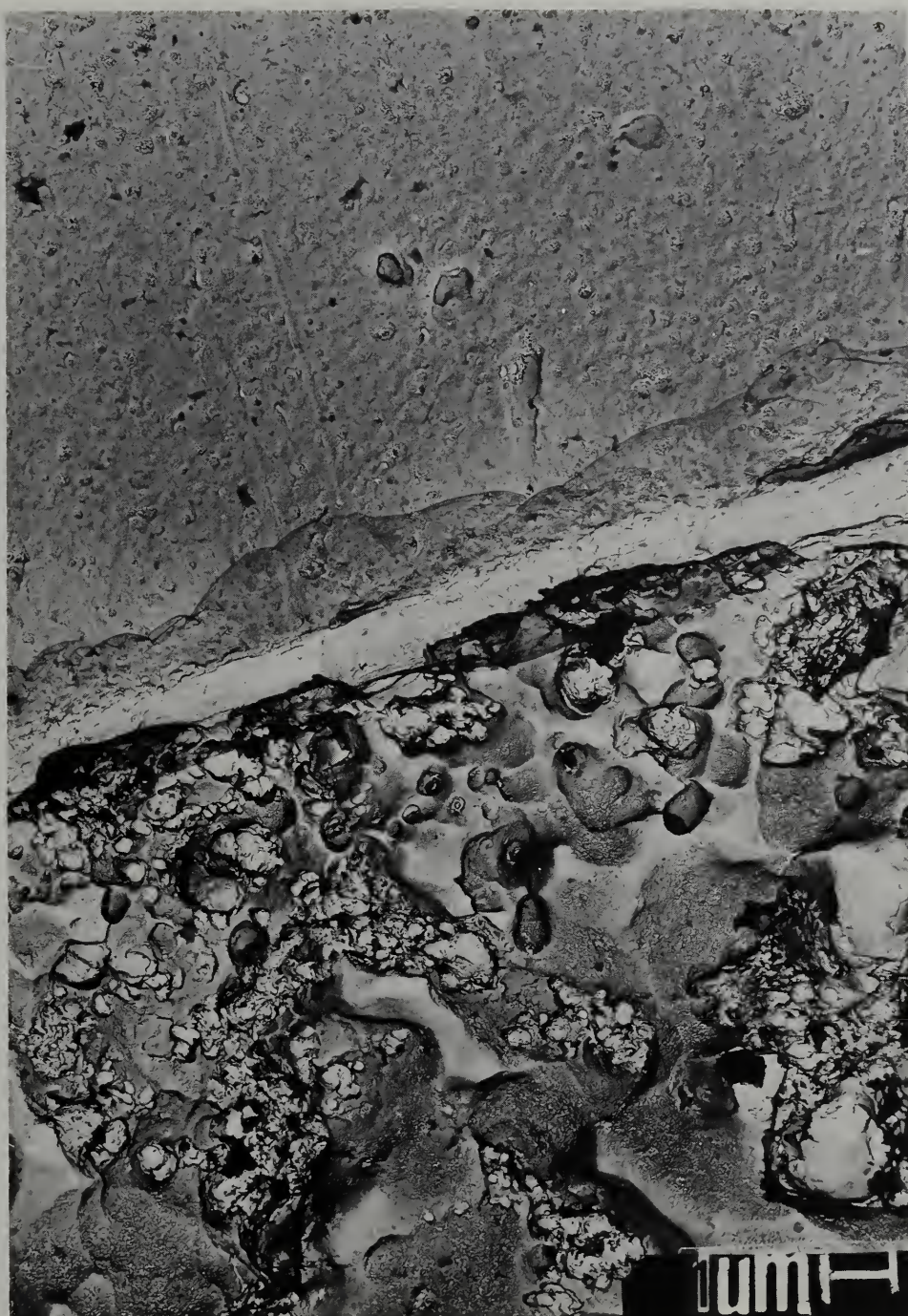


Fig. 3 6,900X. This micrograph illustrates 6061 pre-heated only before enameling and exhibiting moderate spalling. The etch was the same as in Fig. 2. There appears to be an intermediate layer between the enamel and the metal.

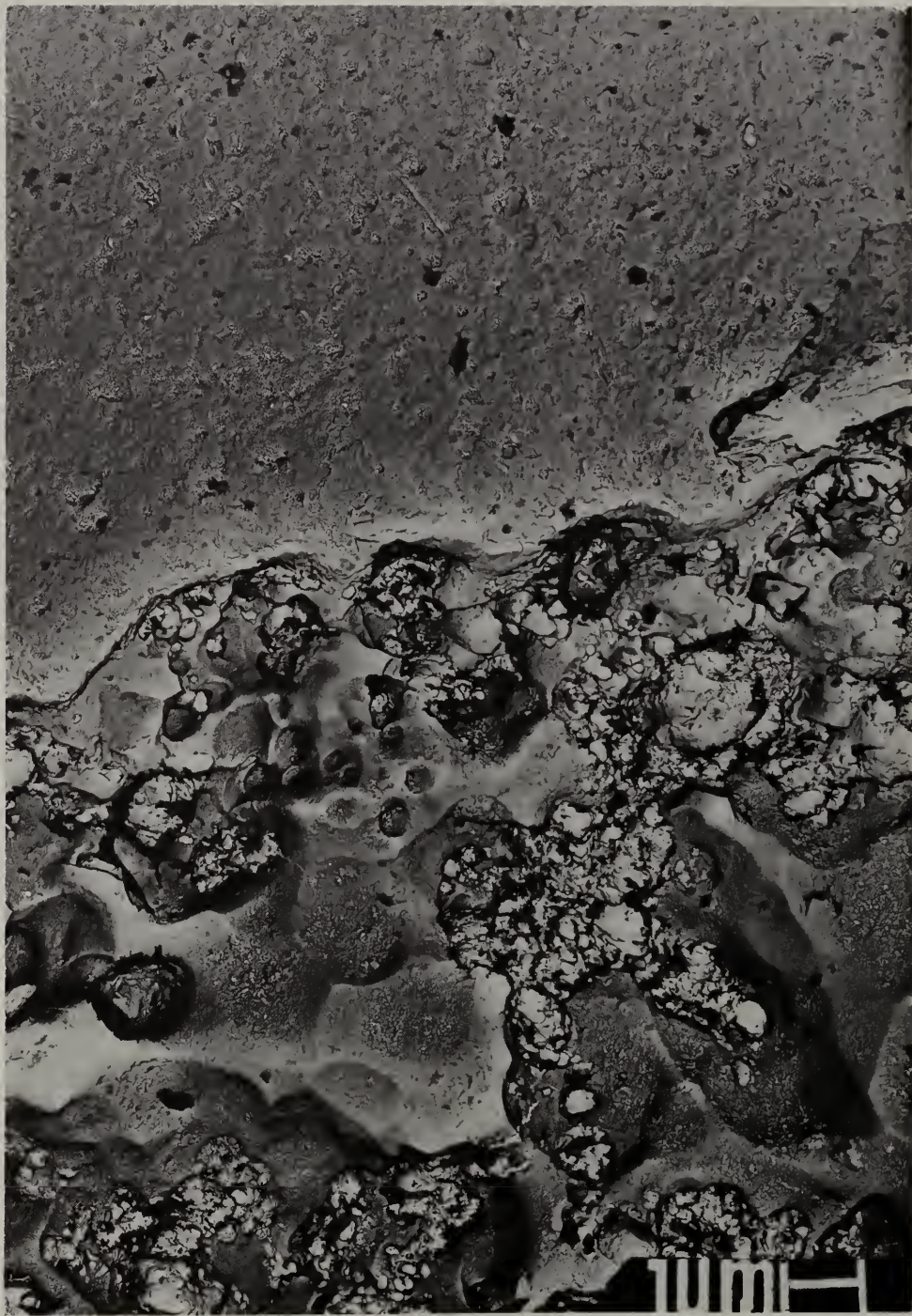


Fig. 4 7,000X. Another area of the replica shown in Fig. 3. This illustrates the variation in the interface structure.

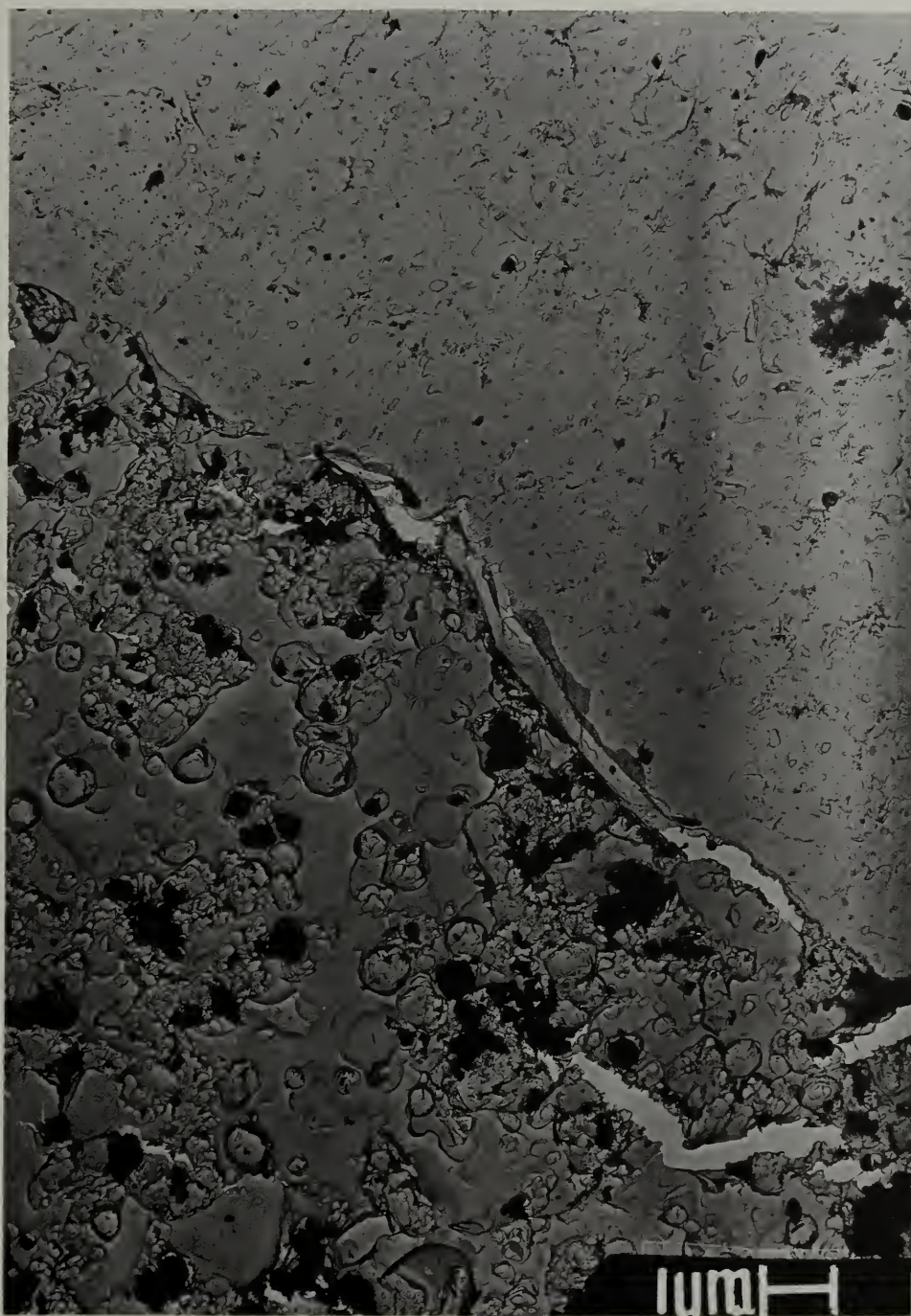


Fig. 5 6,900X. This replica was taken from 6061 preheated only before enameling, which exhibited moderate spalling. Etch was the same as in Fig. 1. In places along the interface there is an intermediate layer.

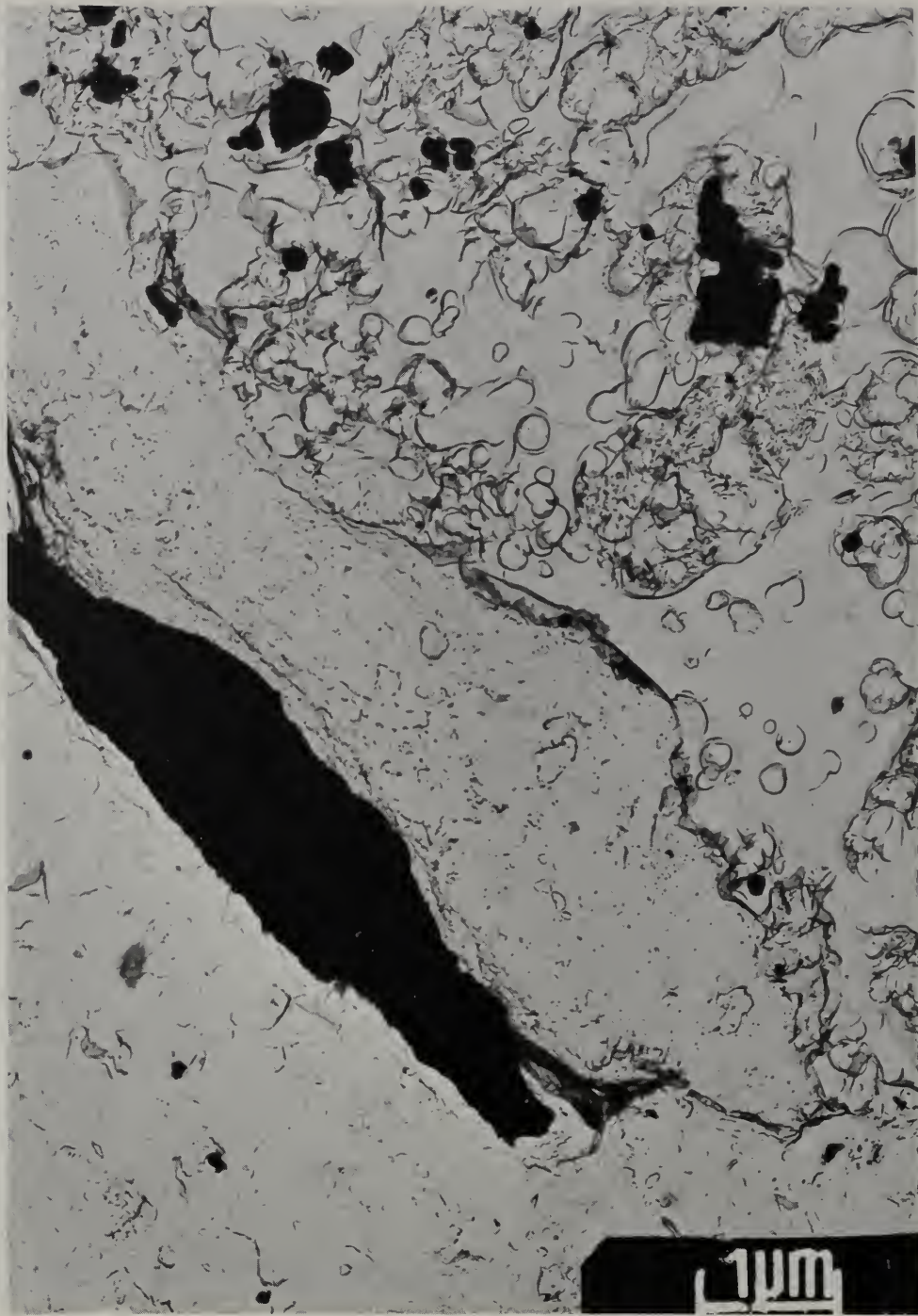


Fig. 6 12,200X. This replica was taken from preheated 5154 which exhibited severe spalling. Note the width of the interface layer here. The black particles are probably extracted material from the specimen surface.

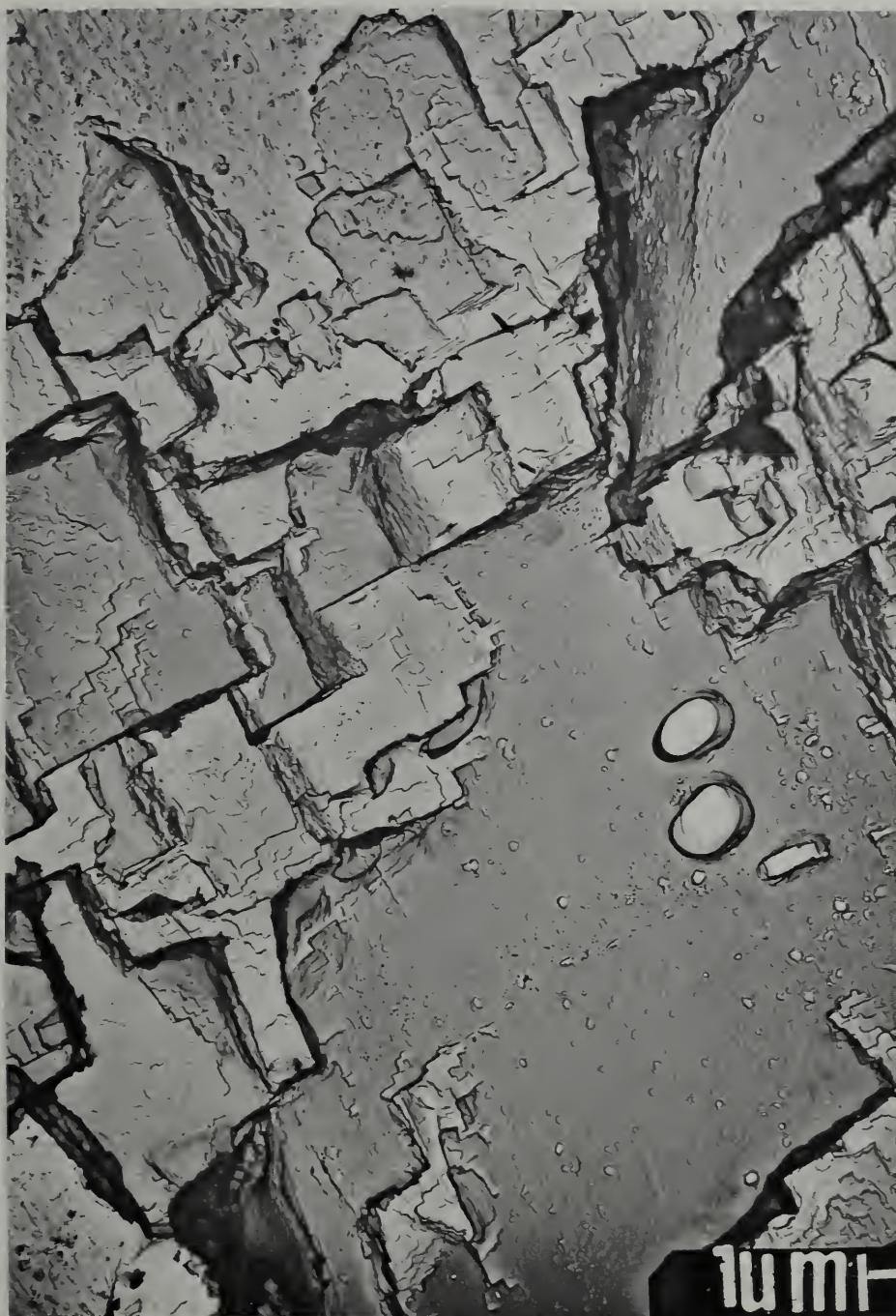


Fig. 7 7,100X. The sample was preheated 1100 exhibiting excellent spall resistance. A double etch technique was used, of 4:1 Keller's Etch for 10 sec. then 1%  $\text{SbCl}_3$  for 4 min. The additional etch was employed to see what effect  $\text{SbCl}_3$  has on the interface area. It can be seen that the metal is severely and preferentially attacked.

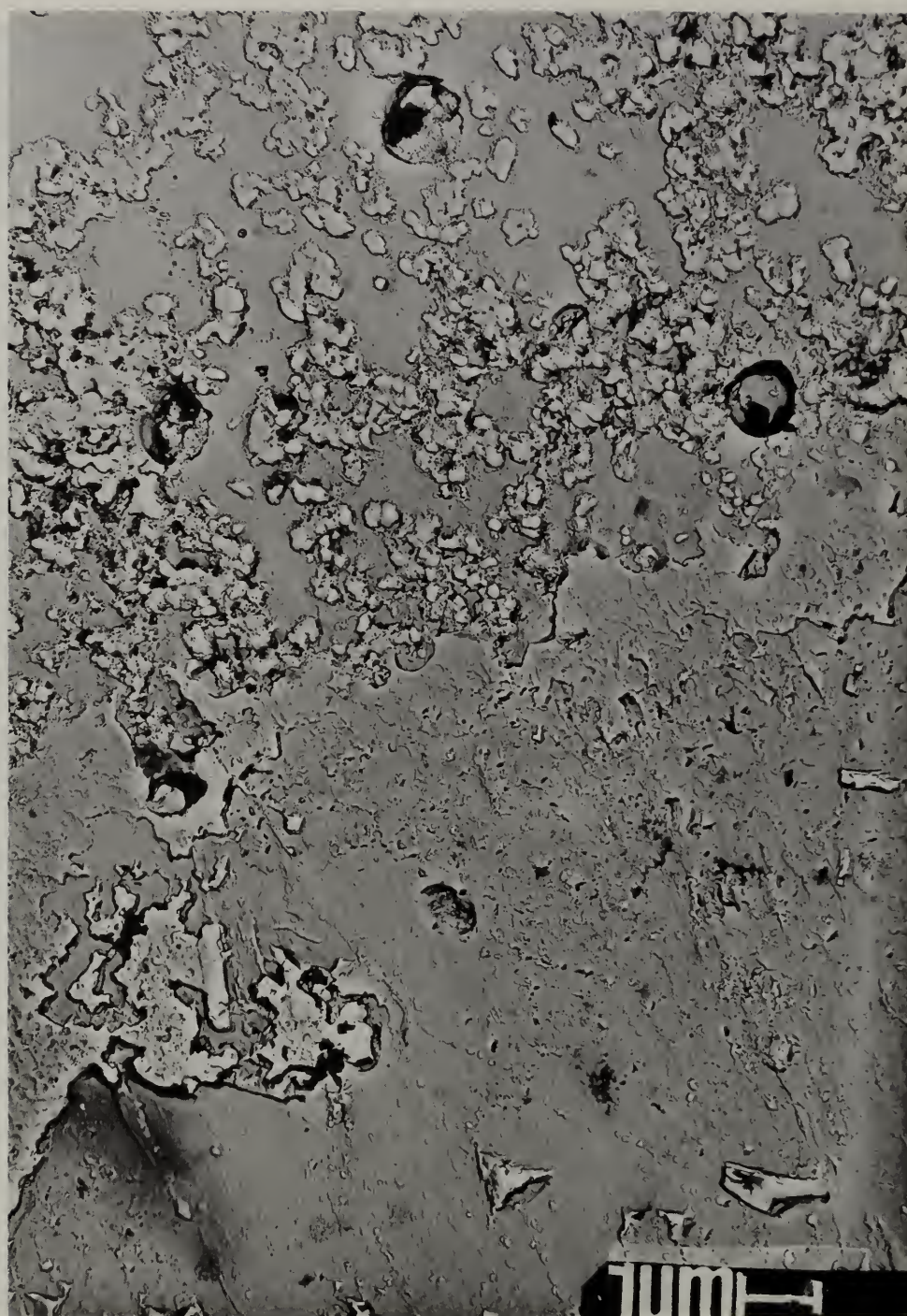


Fig. 8 6,800X. This micrograph was taken in an area immediately above Fig. 7. The original interface appears in the center of the micrograph. The area below this represents porcelain enamel exposed by removal of the aluminum.

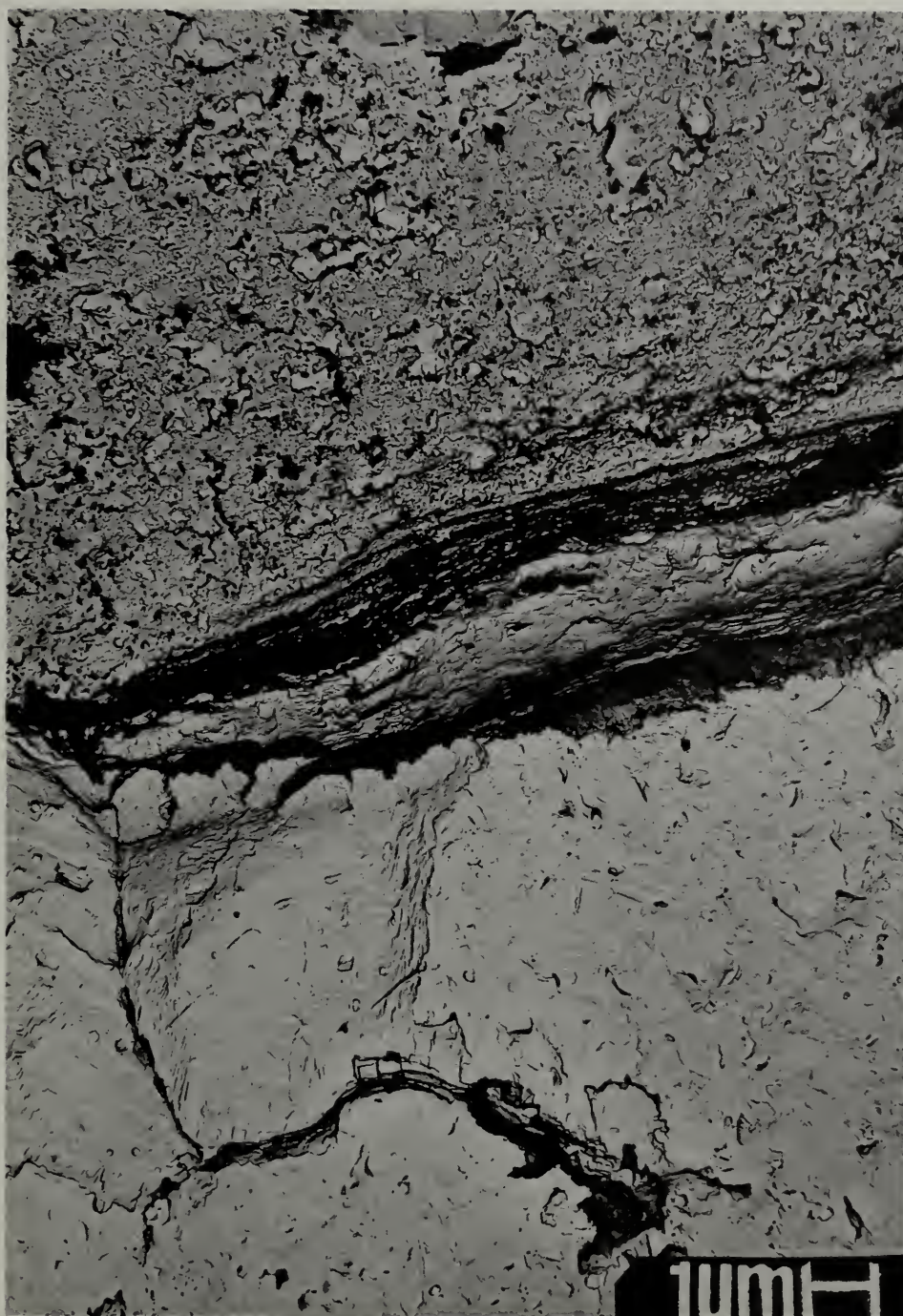


Fig. 9 6,900X. This specimen is 6061 preheated only which exhibits moderate spalling. The double etch technique as described in Fig. 7 was used. Again there seems to be considerable attack in the interface area.

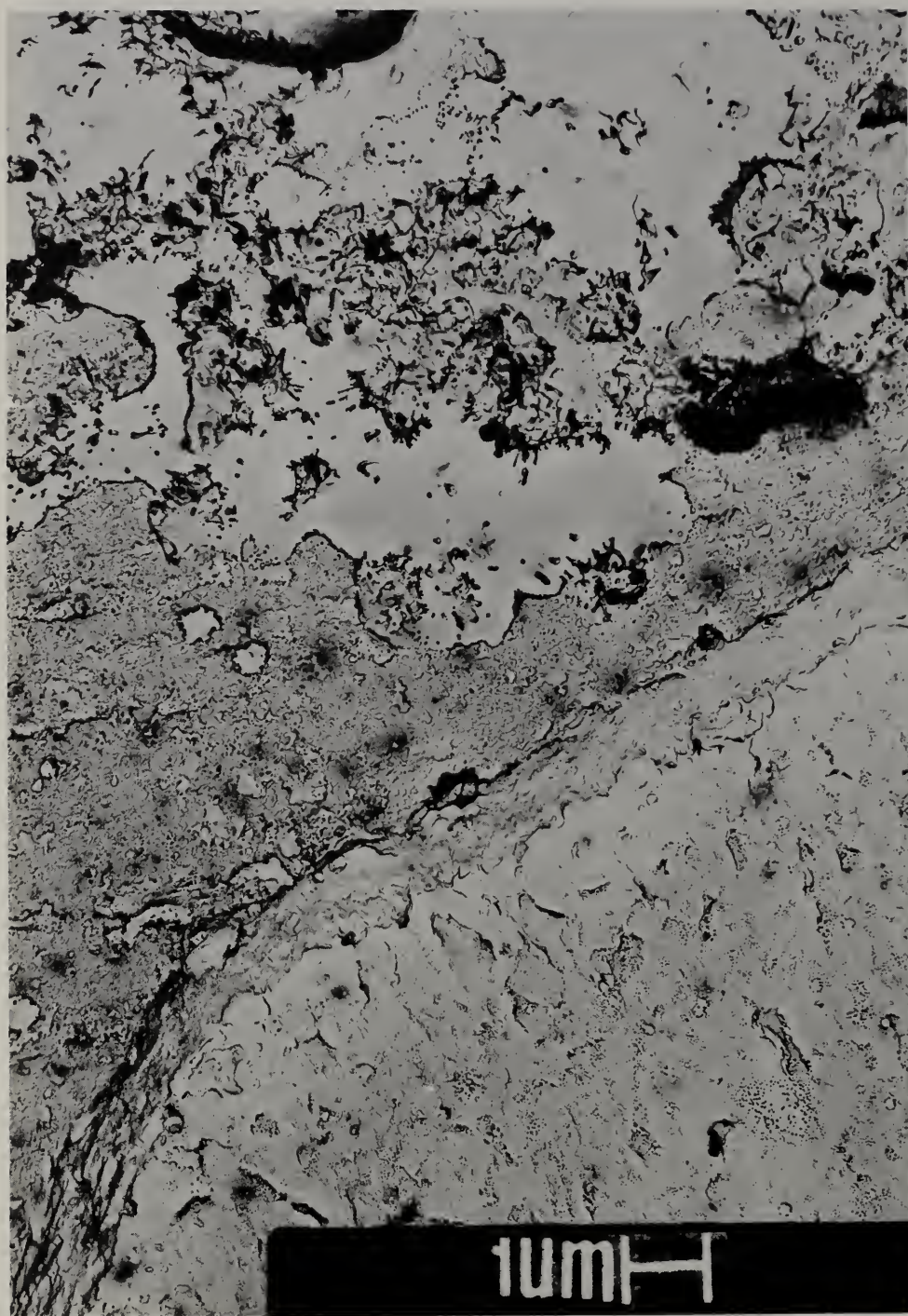


Fig. 10 6,900X. This is another view of pre-heated 6061 with the double etch technique.

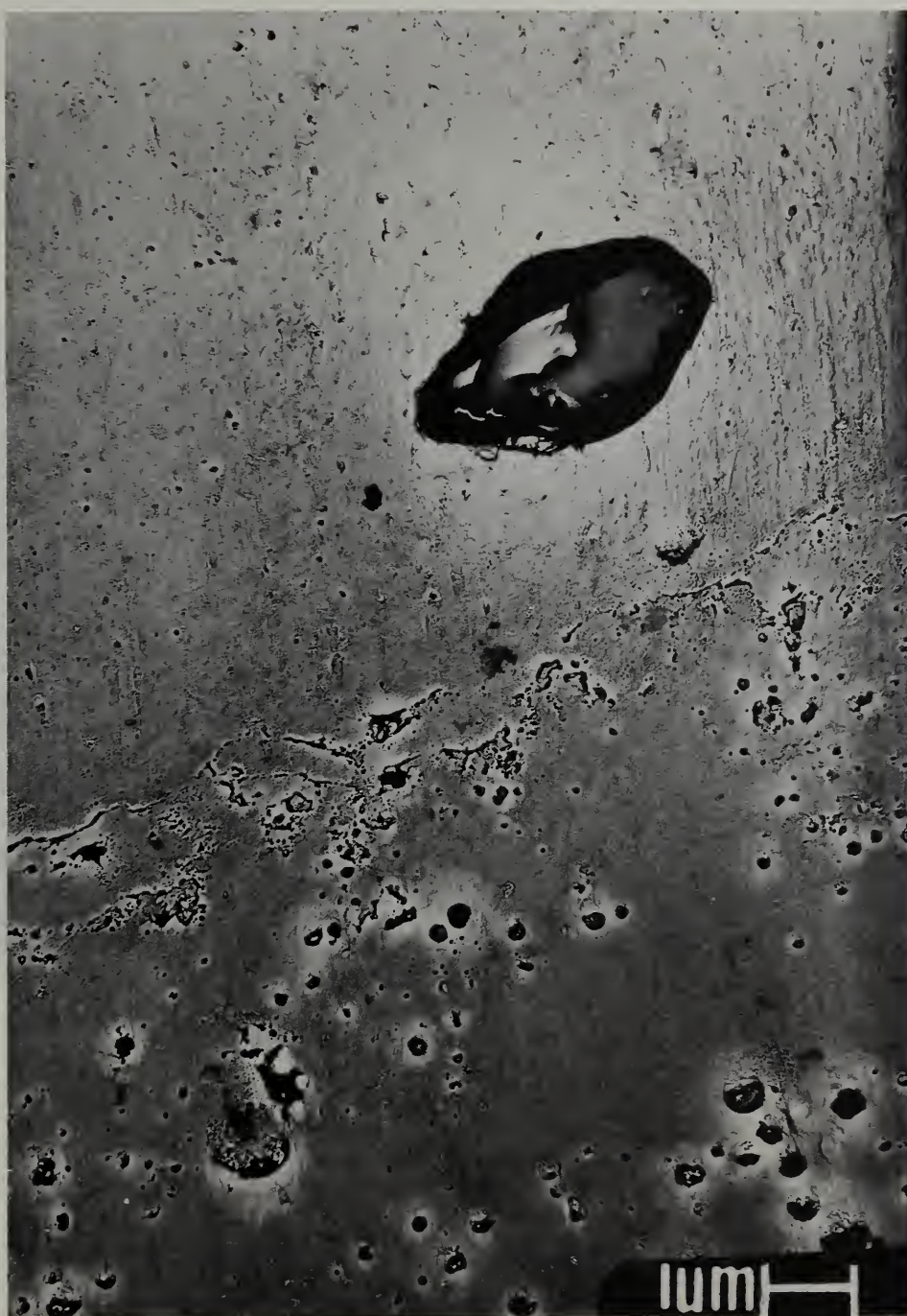


Fig. 11 6,900X. This is 6061 preheated only before enameling. The specimen spalled. The etch used was 1%  $\text{SbCl}_3$  for 15 sec. There seems to be a slight area of attack near the interface, but whether this represents attack of an undissolved interface layer is open to question. A longer  $\text{SbCl}_3$  etch causes much more severe attack at the interface. See Fig. 9 and 10.

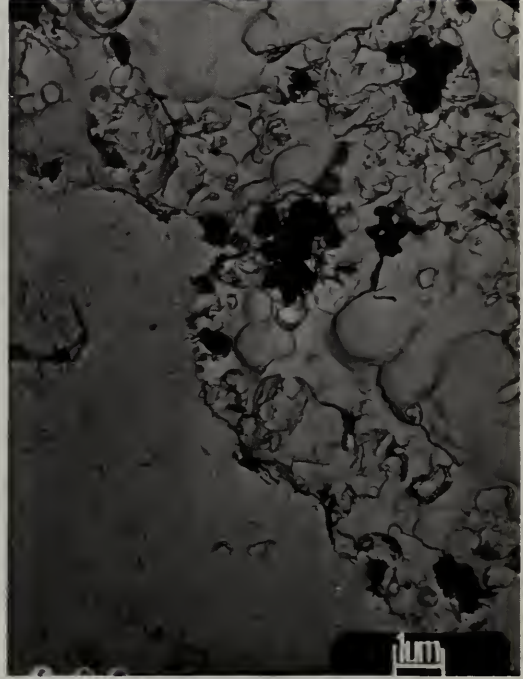
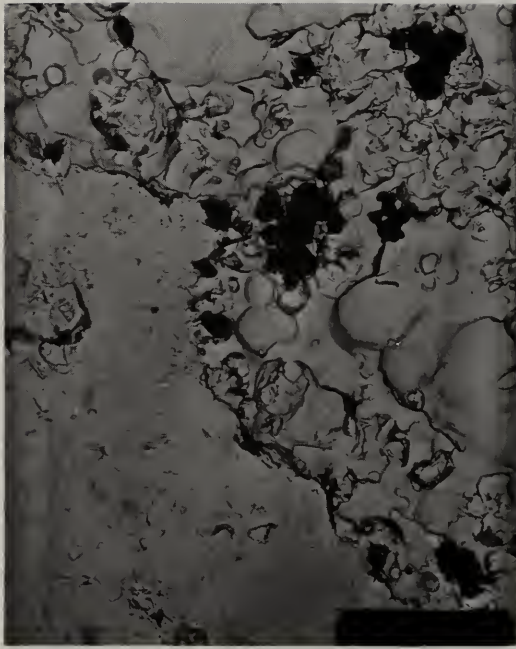


Fig. 12 5,600X. This is pickled 6061. The etch was a 4:1 dilution of Keller's Etch for 10 sec. Compare this with Fig. 1.

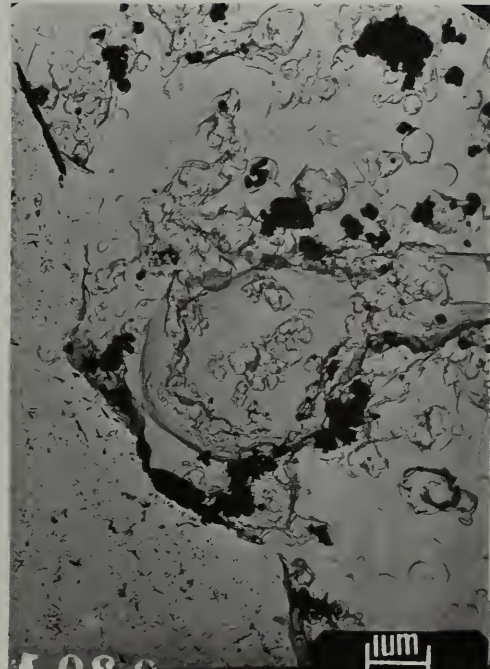
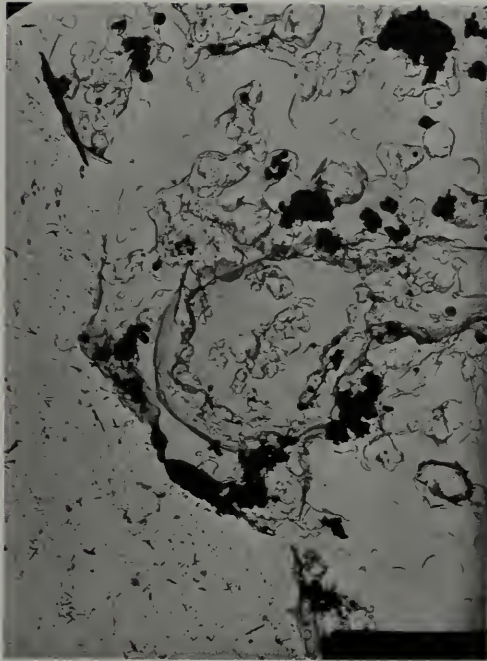


Fig. 13 5,600X. This is 6061 preheated only before enameling. The etch was a 4:1 dilution of Keller's Etch for 10 sec. Compare this with Fig. 5.

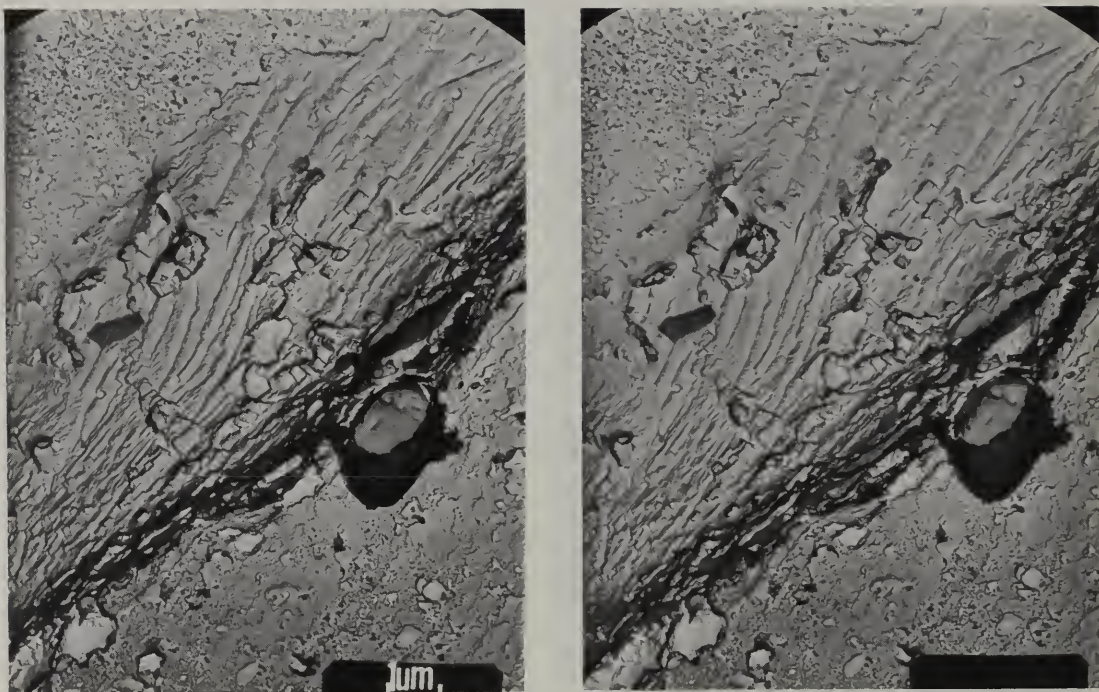


Fig. 14 5,600X. This is preheated 6061. The double etch of dilute Keller's followed by  $\text{SbCl}_3$  (see Fig. 7) was used. Compare this stereo micrograph with Figs. 9 and 10.

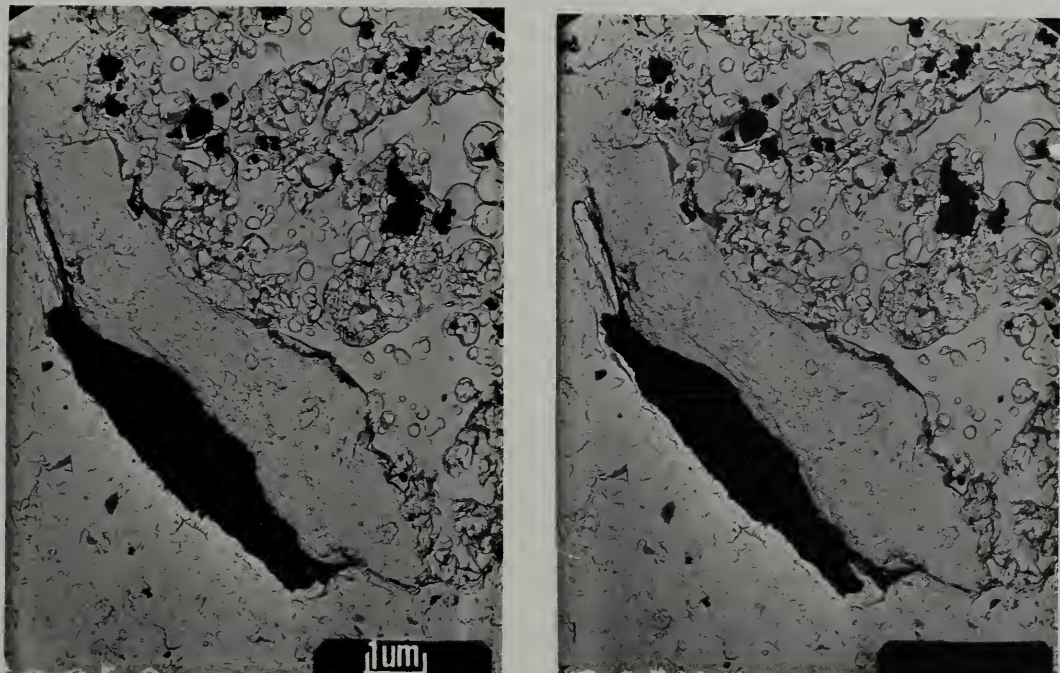


Fig. 15 5,600X. This is 5154 preheated only before enameling. The etch was a 4:1 dilution of Keller's Etch for 10 sec. Compare this with Fig. 6.





