NATIONAL BUREAU OF STANDARDS REPORT

9533

PROGRESS REPORT

August 1, 1966 through April 30, 1967

THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

by

Albert L. Gugeler
Research Associate

Sponsored by

FERRO CORP.

PORCELAIN ENAMEL INSTITUTE RESEARCH ASSOCIATESHIP

NATIONAL BUREAU OF STANDARDS

WASHINGTON, D. C.

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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I INTRODUCTION

The Porcelain Enameled Aluminum Council of The Porcelain Enamel Institute has initiated this Research Associateship Program at The National Bureau of Standards to study the basic mechanism of adherence of porcelain enamel to aluminum. The primary technical problem facing the porcelain enameled aluminum industry is the problem of spalling. This phenomenon involves the flaking or chipping off of the porcelain enamel from the aluminum substrate thereby destroying the integrity of the coating and exposing bare metal. While spalling may occur at any time after the porcelain enamel has been fired, it usually occurs after being exposed to weathering for various periods of time. Spalling is not usually a problem with commercially pure aluminum and with a few selected alloys; also by properly pretreating the metal prior to porcelain enameling, several other alloys can be enameled with confidence. Unfortunately, however, many otherwise desirable alloys cannot be enameled with consistently good results. Furthermore, there is currently no test for predicting the spall resistance of porcelain enameled aluminum with 100% accuracy. Thus it is felt that if the basic mechanism of adherence is understood, and further, if the nature and cause of spalling failure are also understood, then the industry can develop a reliable test for spall resistance.

II SUMMARY

A number of alloys of varying compositions were selected for examination. The initial choices were two magnesium-free alloys, 1100 and 1199, and two magnesium-bearing alloys, 5257 and 5657. Later, various other alloys were added to the program, including 6061 containing magnesium silicide, and 5154 and 5086 with relatively high magnesium contents. Specimens of these alloys were enameled with a conventional aluminum enamel and tested for spall resistance using the antimony trichloride spall test procedure. Polished metallographic cross sections of these specimens were examined with the light microscope, the electron microscope and the electron microprobe, but none of these techniques have as yet led to a definite isolation or identification of a reaction or diffusion zone if any is present. If a diffusion or reaction zone is present at the interface, an understanding of the reactions taking place here should shed considerable light on the mechanism of adherence and or the reasons for spalling. The electron microprobe scans have shown however, that in general, magnesium-bearing alloys form a magnesium rich layer at or near the interface when subjected to elevated temperatures such as occur during the prefire cleaning treatment of the metal, or the firing of the porcelain enamel. This magnesium concentration has been substantiated by analyses of the oxide film formed on the surface of the alloys after prefiring. Analyses show the oxide layer to be richer in magnesium than the body of the alloy. Oxide analyses also show a variation in oxide thickness after prefiring when various alloys are compared. This might also have a bearing on the problem, as these variations do not correlate completely with magnesium content of the alloys. Magnesium introduced on the surface of alloy 1100 by vapor deposition causes this alloy to exhibit spalling. This fact indicates that the poor spall resistance of magnesium bearing alloys may be due to a high magnesium concentration at the surface. Chromium vapor deposited on top of this artificially introduced magnesium layer and also vapor deposited on normally badly spalling alloys alleviates this condition markedly.

III DISCUSSION AND RESULTS

Originally four alloys were chosen to start the program. Two magnesium-free alloys, 1100 and 1199 were selected along with two alloys, 5257 and 5657, which contain magnesium. Spall resistance as measured by the antimony trichloride spall test did show some spall failures on both of the magnesium-bearing alloys. More failures occurred on 5657, but the degree of spall and the consistency of its occurrence was such that it was felt that an alloy exhibiting more severe failure would be of advantage. For this purpose, alloys 5154 and 5086 were added to the program. Both are relatively high in magnesium content (see Table #1 for a comparison of all alloys considered thus far in the program) and spall very badly when tested in the above manner.

A number of photomicrographs were taken of various alloys after enameling. Magnifications up to 875X failed to reveal any definitely identifiable zone of reaction in the interface area. In several instances, what appeared to be banded zones at the interface were later concluded to be due to relief occurring during the polishing of the samples. See figures 26 and 27 for examples of light micrographs.

Cross-section samples were submitted for electron microprobe analysis of the interface. Initially samples of 1100 and 6061 were submitted. Both alloys had been chemically cleaned for seven minutes and then subjected to an R-100 [1.] bath for ten minutes prior to enameling. The 1100 sample exhibited good spall resistance and the 6061 sample exhibited failure. Both samples were tested using the antimony trichloride spall test. Traces for all the elements contained in the two samples showed no marked difference, so a sample of prefired 5154 alloy was added and traces of the elements aluminum, magnesium, lead and silicon were obtained. Figures 1-4, 5-8, and 9-12 show these traces on the 1100, 6061 and 5154 samples respectively. As a follow-up to this work, samples of 5154 with a seven minute chemical clean, ten minute R-100 pretreatment prior to enameling, and samples of prefired 6061 and 5657 were submitted and traces were obtained for magnesium, copper and chromium. Figures 13-15, 16-18 and 19-21 show these traces on the 5154, 6061 and 5657 samples respectively. The microprobe shows no evidence of aluminum or other elements diffusing from the substrate into the enamel. However, the resolution of the microprobe is not critical enough to indicate diffusion of less than about 3 1/2 microns since the area being analyzed by the probe is approximately 3 1/2 microns in diameter. Concentrations of magnesium are noted at or near the interface of the magnesium bearing alloys except for the sample of 5154 which had been chemically cleaned and treated with R-100 prior to enameling. 5154 is a magnesium alloy whereas 6061 is a magnesium silicide alloy. The fact that magnesium is more soluble in the R-100 bath than magnesium silicide could account for the disappearance of the magnesium peak on the second sample of 5154 as opposed to the peaks being evident on both of the 6061 specimens.

Specimens of 1100, 6061, 6063, 5154 and 5657 in the as-received and prefired condition were submitted to the participating aluminum manufacturers for determination of oxide thickness and composition. Results to date substantiate the microprobe findings insofar as magnesium enrichment is concerned. After oxidation by prefiring, the oxide layer of the magnesium bearing alloys contain a higher proportion of magnesium than would be expected by chemical composition of the alloy alone. This would indicate preferential diffusion of magnesium from the body of the alloy into the oxide layer as it increases in thickness due to heating. Several literature references make mention of this. [2. 3. 4.] It is stated in the literature on this subject, that in aluminum-magnesium alloys, if the alloy is heated above 350 degrees C (660 degrees F), (which is below the temperature of prefire cleaning or enameling) a film

of magnesium oxide forms on the surface of the alloy. Of interest also, is the variation in oxide thickness from alloy to alloy. It has been suggested by others that perhaps enamelability depends not only on the amount of magnesium oxide formed on heating but also on the amount formed in proportion to the total amount of all oxide formed. This might explain the enameling characteristics of 6061 vs. 6063, which although similar in alloy composition do not have the same oxide film characteristics or enamelability. The oxide thickness measurements and compositions received to date are summarized in Tables 2. and 3.

In order to study the magnesium film phenomenon further, thin films of magnesium of varying thickness were vapor deposited on 1100. The specimens were then prefired and enameled. The smallest amount of magnesium deposited on the surface caused spalling, and the severity of the spall increased as the amount of magnesium vapor deposited on the alloy increased. Depositions ranged from approximately 0.01 to 0.09 grams per square foot. If after vapor depositing magnesium on 1100, a coating of 0.02 grams per square foot of chromium was vapor deposited on top of the magnesium coating, the specimen then exhibited no spalling. With this in mind, chromium was vapor deposited in amounts varying from approximately 0.01 to 0.10 grams per square foot on alloy 5086. After subsequent prefiring and enameling, these specimens showed a marked improvement in spall resistance, although all specimens still failed. Increasing the thickness of the chromium deposit was beneficial only to a certain point; beyond this point thicker coatings gave no further help. Copper and iron were also vapor deposited on 5086. While these coatings also helped to minimize spalling, they were not as effective as chromium.

Another technique used for studying the enamel-aluminum interface was electron microscopy. Palladium-shadowed plastic replicas were taken of the surface of tapered sections of enameled 1100 and 5154. The initial replicas were exploratory and are inconclusive. Nevertheless, several photomicrographs using this technique are shown in Figures 22-25. Figures 22 and 23 are of enameled 1100 at a magnification of 4KX. The angle of taper is approximately 5 degrees from parallel to the interface. This would effectively enlarge any band of diffusion zone approximately 15 times normal thickness. There is no sharp delineation between the enamel and the aluminum in these figures. While this might indicate diffusion, it must be kept in mind that there was no attempt made at selective etching following polishing. This might possibly lead to erroneous conclusions. Figure 24 is a sample of enameled 1100 which was etched with 80% phosphoric acid, 10% nitric acid and 10% water at 90 degrees C for two minutes following polishing. (The dark segments are caused by tearing and subsequent folding of the plastic replica in localized areas.) Figure 25 is enameled 5154 which also has been etched after polishing. The replica is badly torn at the interface area, making interpretation of this micrograph difficult.

REFERENCES:

1. R-100 Chemical Pretreatment Pat. No. 2,719,796 (Aluminum Company of America). A chromic acid-sulfuric acid bath used to deoxidize or desmutt the aluminum alloy surface.
2. L. de Brouckere, J. Inst. Metals, 1945, 71,131
3. W. W. Smeltzer, J. Electrochem. Soc., 1958, 105, 67
4. R. A. Hine and R. D. Gominski, J. Inst. Metals, 1960-61, 89, 417

TABLE # 1

ALLOYS CONSIDERED IN PROGRAM

ALLOY	SPALL RESISTANCE	COMPOSITION
1100 (1)	Excellent	Al-99.150 Cu-0.150 Mn,Zn-0.020 ea. Fe- 0.510 Si-0.120 Ti,V,Ga-0.010 ea.
1100 (1)	Excellent	Al-99.17 Cu-0.12 Ti-0.01 Fe- 0.60 Si-0.10
1199 (1)	Excellent	Al-99.992 Cu-0.003 Si- 0.004 Fe,Ga-0.002 ea.
3003 (2)	Generally good to excellent	(3)Al-96.75 Fe-0.7 max Zn-0.10 max. Mn- 1.0-1.5 Si-0.60 max. Cu- 0.20 max. Max. ea. of other 0.05 with 0.15 max.
6061 (2)	Can range from good to bad depending on pretreatment.	(3)Al-95.8 Si-0.4-0.8 Cu-0.15-0.40 Mg-0.8-1.2 Cr-0.15-0.35 Fe-0.7 max. Zn-0.25max Mn,Ti-0.15 max ea. Max. ea. of other 0.05 with 0.15 max.
6063 (2)	Can range from good to bad. Generally not recommended.	Al-98.77 Si-0.44 Fe-0.23 Mg- 0.54 other less than 0.01 ea.
5257 (1)	One failure noted. Might be enamelable with proper metal pretreatment.	Al-99.532 Mg-0.28 Fe-0.070 Si- 0.04 V -0.01 Cu,Zn,Ti-0.02 ea. Mn-0.005 Ni-0.003
5657 (1)	Approx. 50% of samples failed the spall test.	Al-99.02 Mg-0.79 Cu-0.06 Si,Fe-0.04 ea. Zn-0.02 Mn,Ni,Cr,Ti less than 0.01 ea.
5154 (1)	Extremely poor.	Al-95.93 Mg-3.5 Cr-0.26 Fe-0.19 Si-0.10 Mn-0.01 Other less than 0.01 ea.
5086 (1)	Extremely poor.	Al-95.18 Mg-3.89 Mn-0.48 Fe- 9.22 Si-0.10 Cr-0.09 Cu-0.02 Ti,Zn,Ni less than 0.01 ea.

(1) Tested during this program; preheat cleaning only; $SbCl_3$ spall test
(2) Based on general industry experience
(3) Nominal composition

TABLE # 2

COMPARISON OF ANALYSIS OF OXIDE THICKNESS

ALLOY	SOURCE # 1 Thickness (angstroms)	SOURCE # 1 Increase	SOURCE # 2 Thickness (angstroms)	SOURCE # 2 Increase	SOURCE # 3 Thickness (mils)	SOURCE # 3 Increase
1100_1	160	60	190	107	-	0.040
1100	220		297		-	
5657_1	110	290	233	344	-	0.097
5657	400		577		-	
6061_1	240	380	393	447	-	0.040
6061	620		840		-	
6063_1	220	120	420	107	-	0.067
6063	340		527		-	
5154_1	220	270	813	497	-	0.052
5154	490		1310		-	
1199_1	Did not receive this alloy		Did not receive this alloy		-	0.067
1199					-	

The subscript following the alloy number means that this particular sample was sent for analysis with only its naturally occurring oxide film.

Those samples that do not have a subscript number were oxidized for 10 minutes at 1000 degrees F.

The above figures are condensed from analyses performed by Alcoa, Alcan and Kaiser aluminum companies.

TABLE # 3

COMPARISON OF ANALYSIS OF OXIDE COMPOSITION

ALLOY	SOURCE # 1 Magnesium (mgs)	SOURCE # 1 Difference (mgs)	SOURCE # 2 Magnesium (mgs)	SOURCE # 2 Difference (mgs)
1100_1	0.00	0.00	0.04	-0.03
1100	0.00		0.01	
5657_1	0.11	0.49	0.09	0.69
5657	0.60		0.78	
6061_1	0.34	0.64	0.47	0.83
6061	0.98		1.30	
6063_1	0.00	0.51	0.06	0.77
6063	0.51		0.83	
5154_1	0.37	0.97	0.78	0.86
5154	1.34		1.64	
1199_1	0.02	0.00	Did not received this alloy	
1199	0.02			

The subscript following the alloy number indicates that this particular sample was sent for analysis with only its naturally occurring oxide.

Those samples not having a subscript number were oxidized for 10 minutes at 1000 degrees F.

The above figures are condensed from analyses performed by the Alcoa and Alcan aluminum companies.

1100 Aluminum Alloy

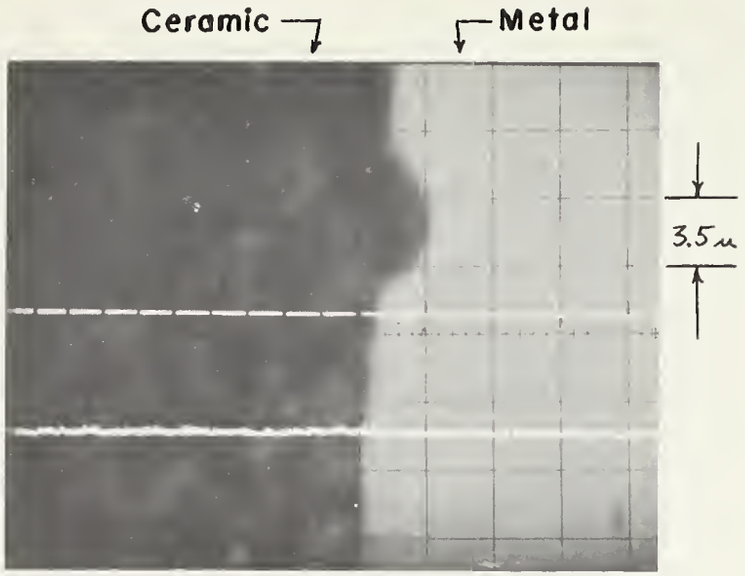


Figure 1. Target Current plus MgKα

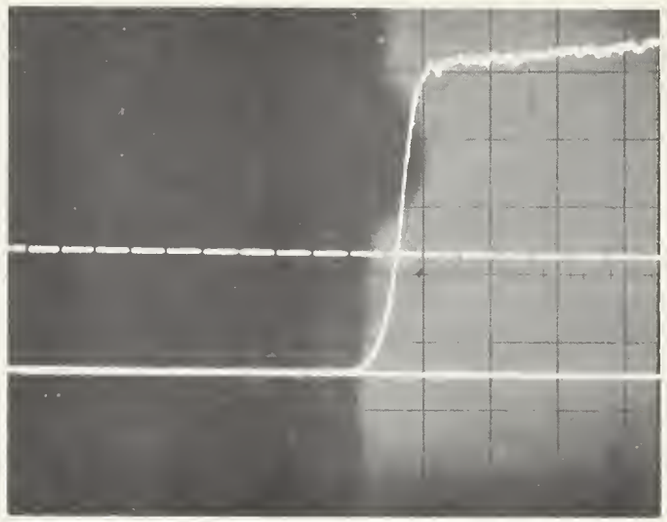


Figure 2. Target Current plus AlKα

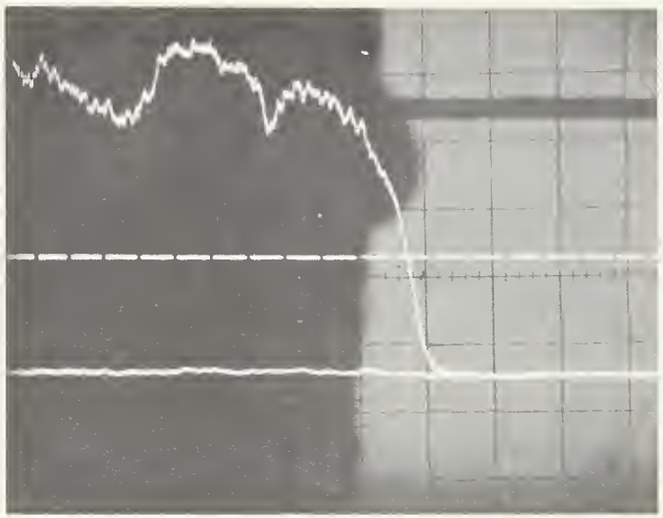


Figure 3. Target Current plus PbLα

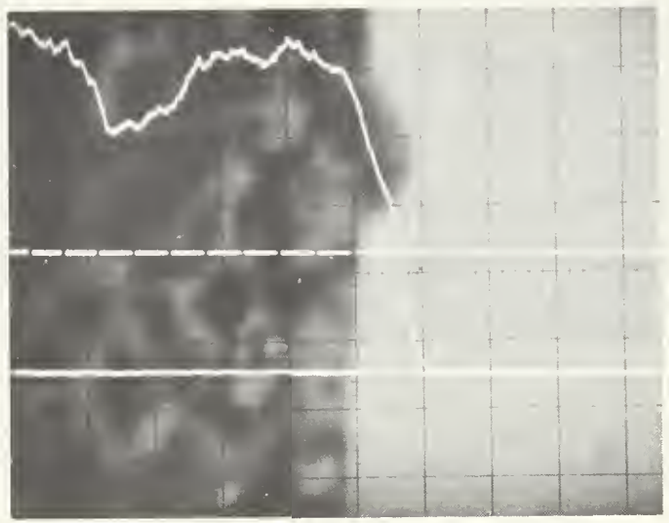


Figure 4. Target Current plus SiKα

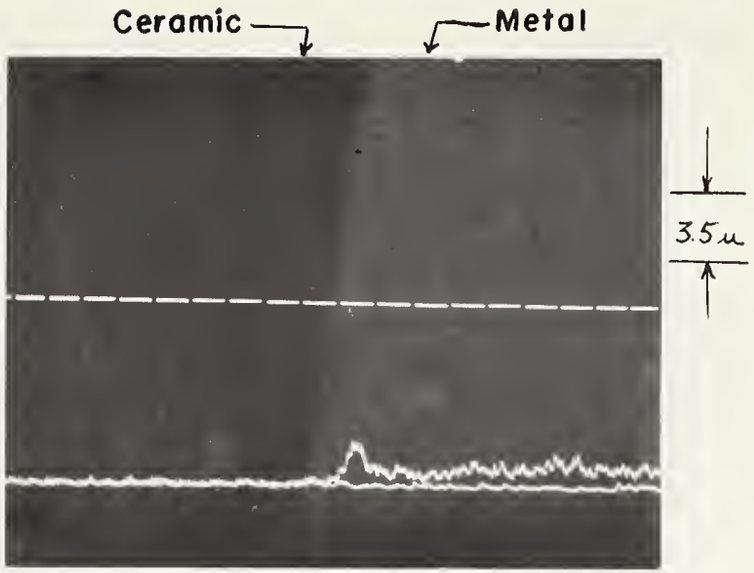


Figure 5. Target Current plus MgKα

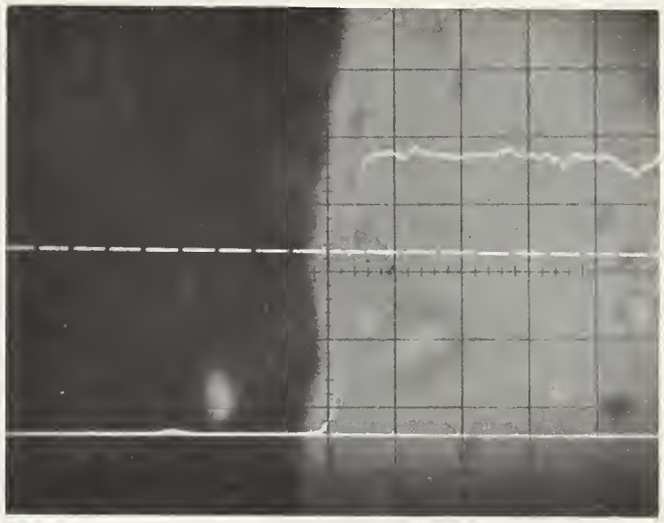


Figure 6. Target Current plus AlKα

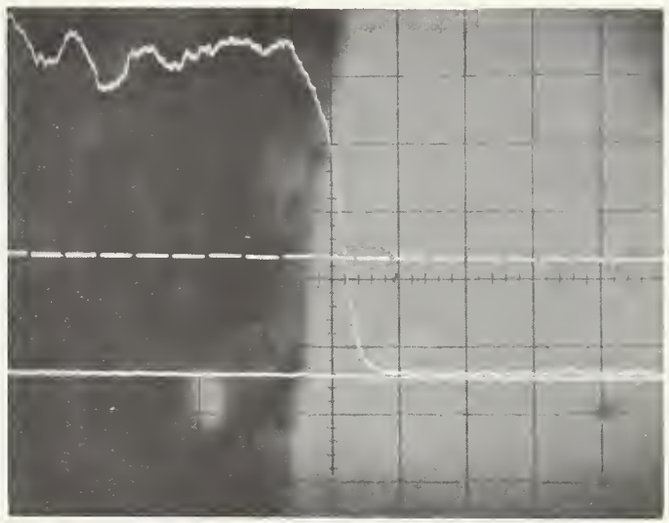


Figure 7. Target Current plus PbLα

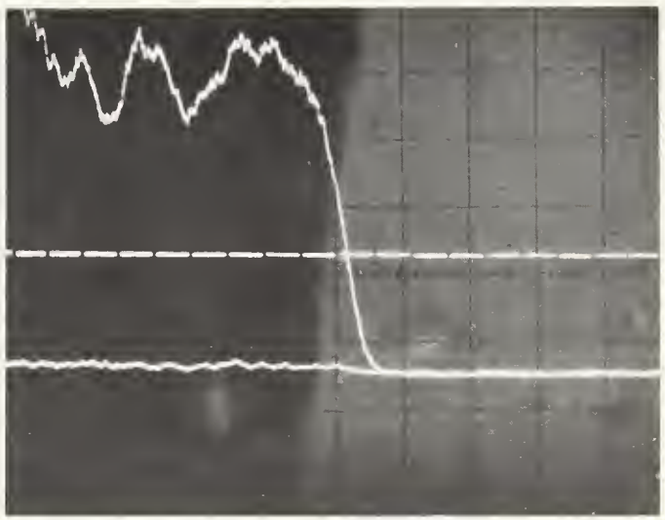


Figure 8. Target Current plus SiKα

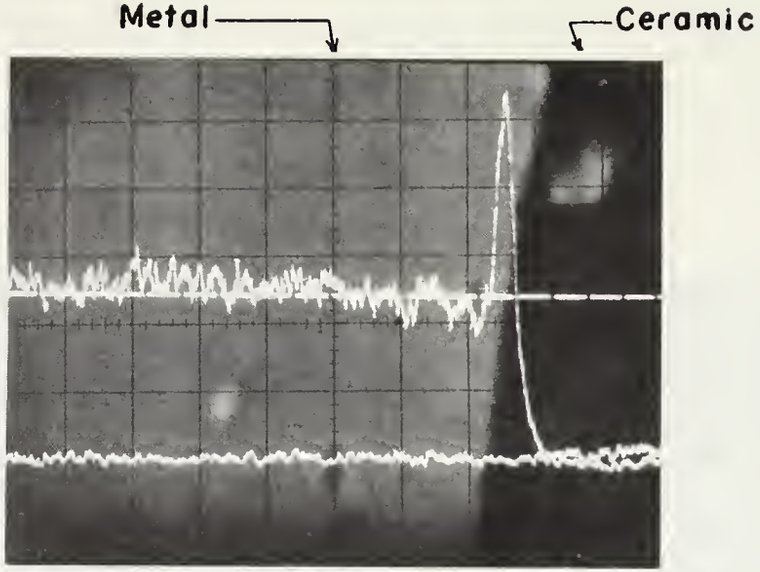


Figure 9. Target Current plus MgKα

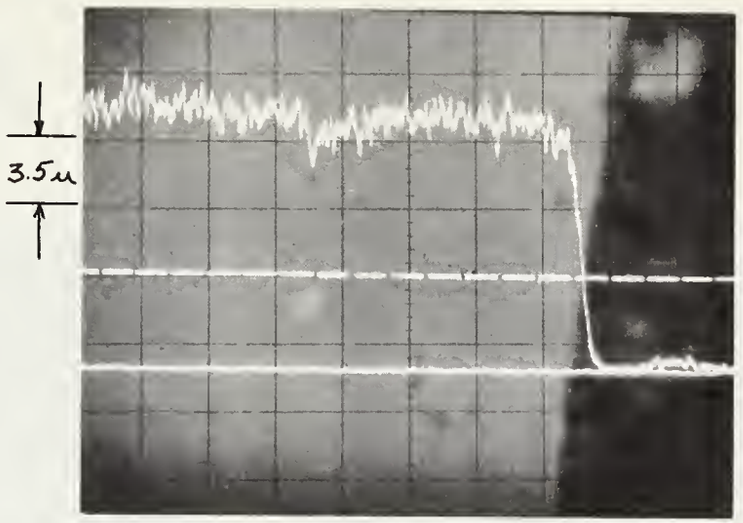


Figure 10. Target Current plus AlKα

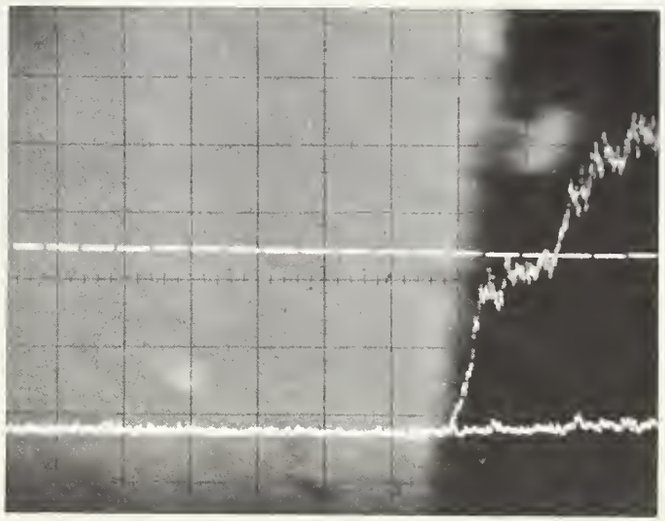


Figure 11. Target Current plus PbLα

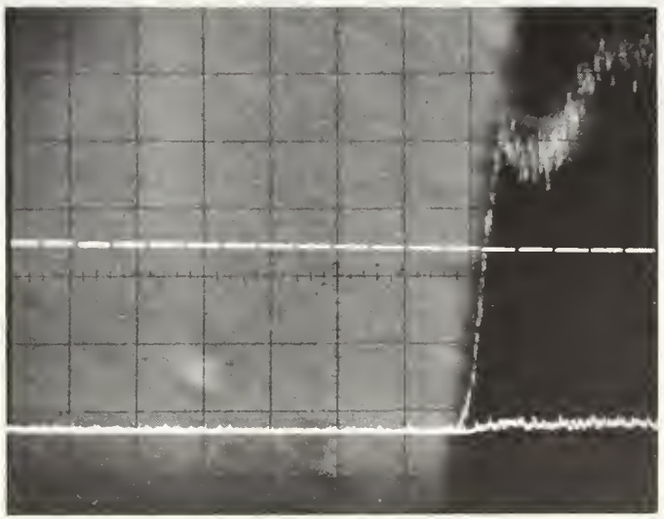


Figure 12. Target Current plus SiKα

5154 Aluminum Alloy

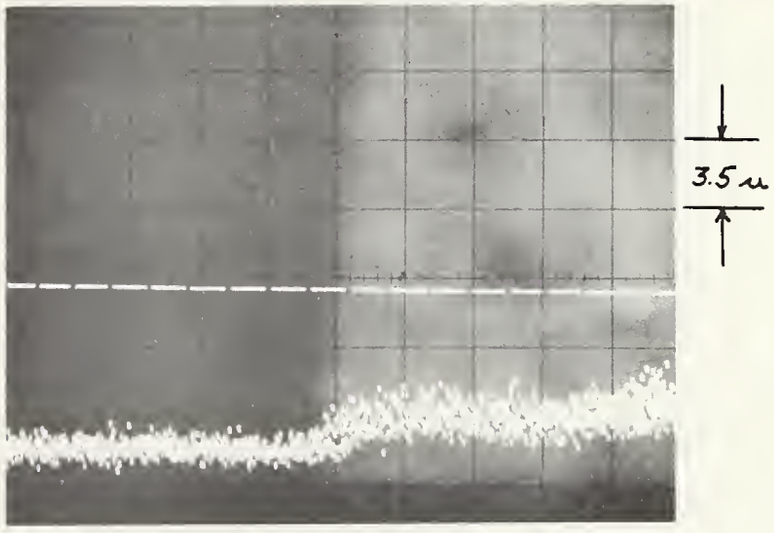


Figure 13 Target Current Plus CuK_α

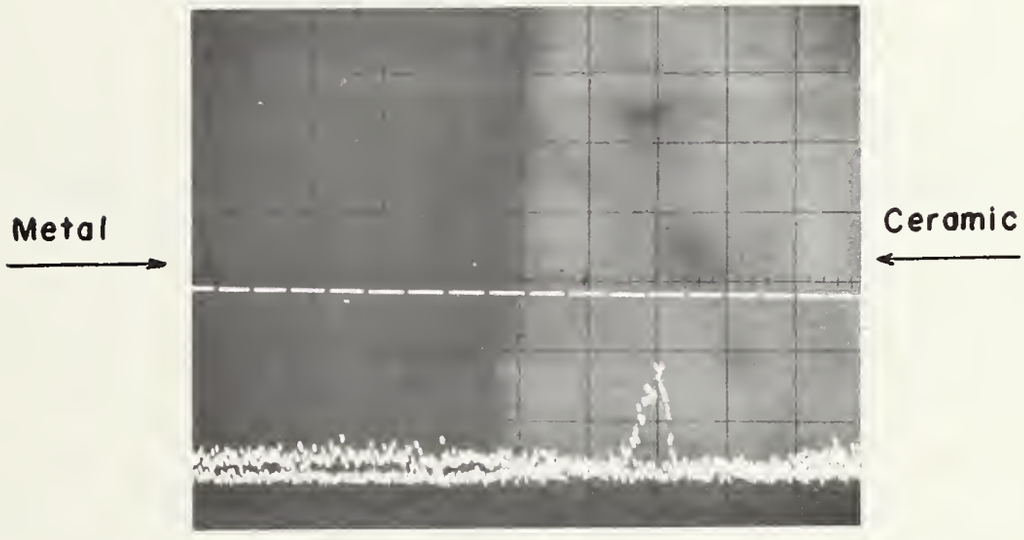


Figure 14 Target Current Plus CrK_α

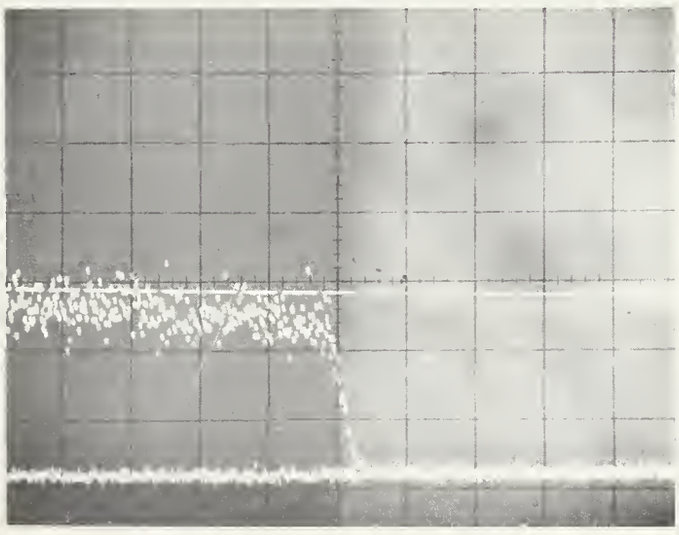


Figure 15 Target Current Plus MgK_α

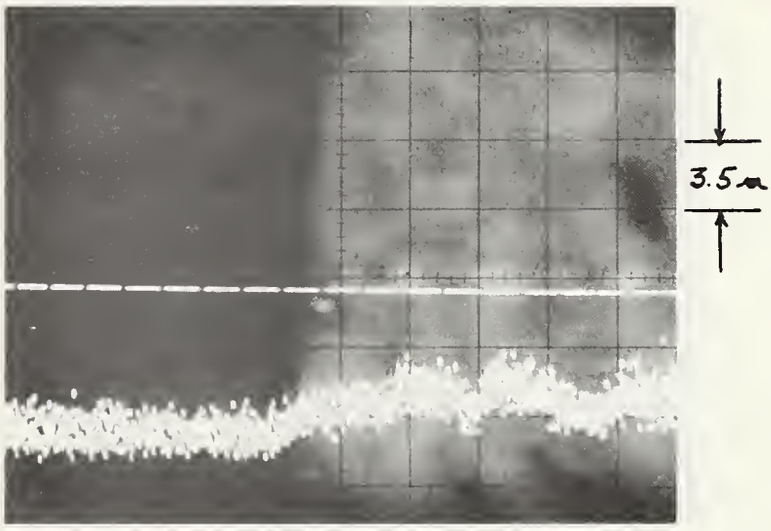


Figure 16 Target Current Plus CuK_{α}

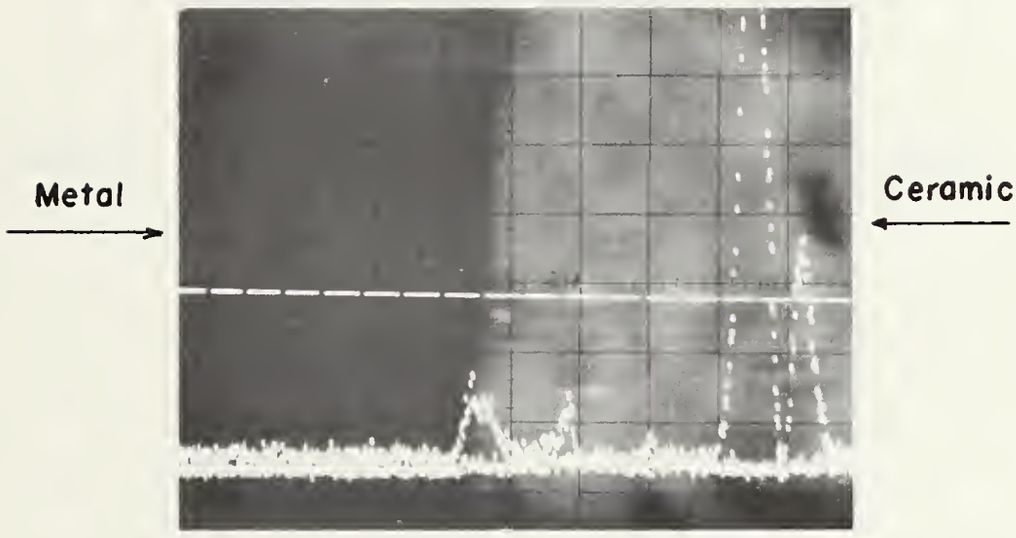


Figure 17 Target Current Plus CrK_{α}

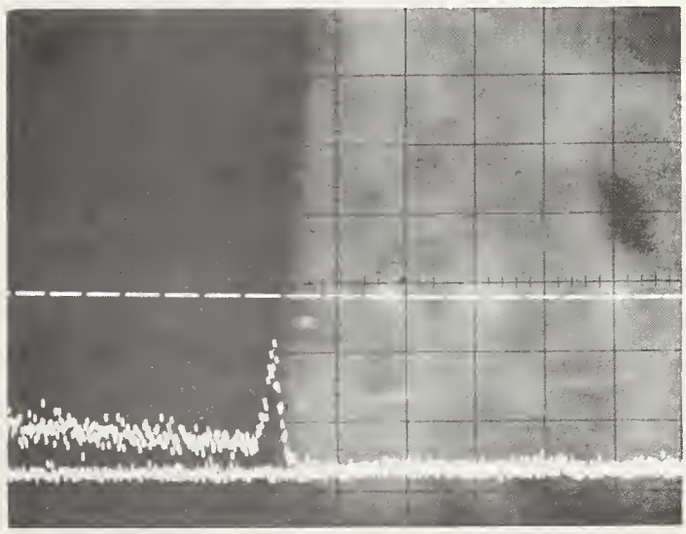


Figure 18 Target Current Plus MgK_{α}

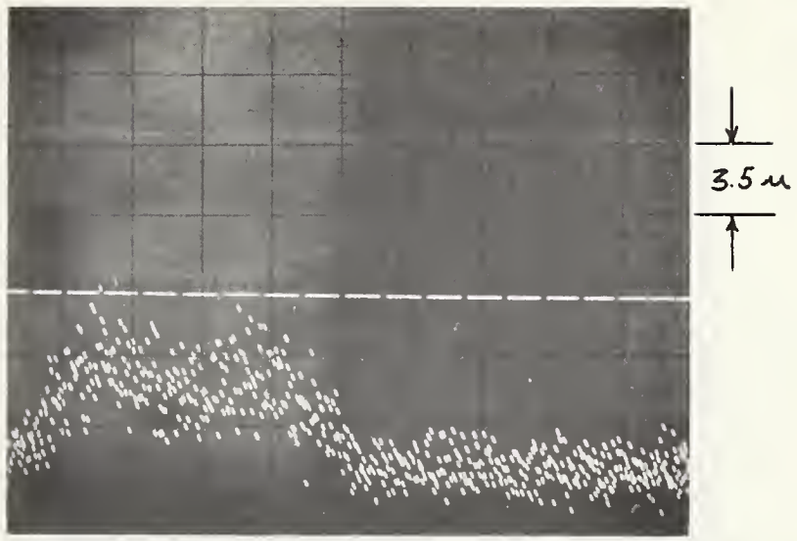


Figure 19 Target Current Plus CuK_α

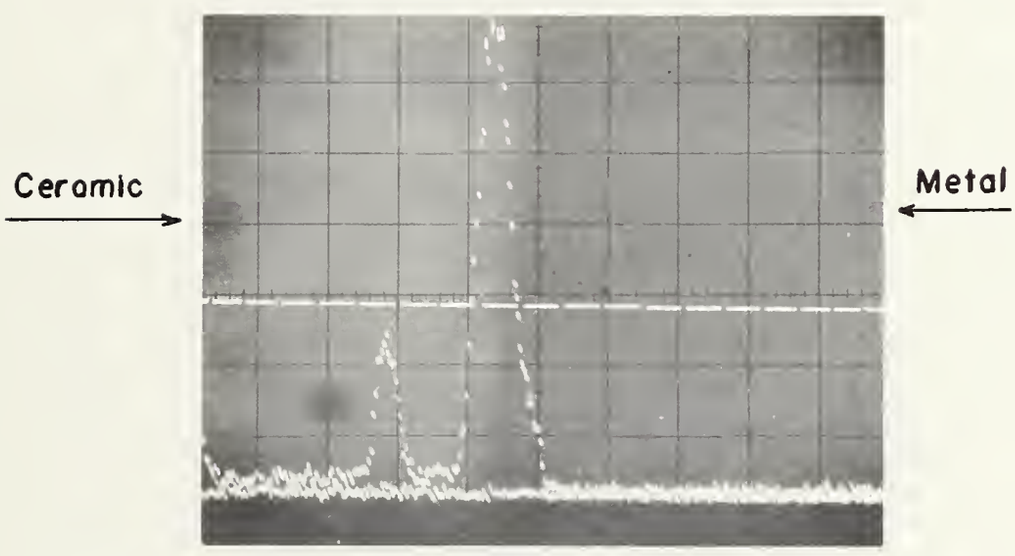


Figure 20 Target Current Plus CrK_α

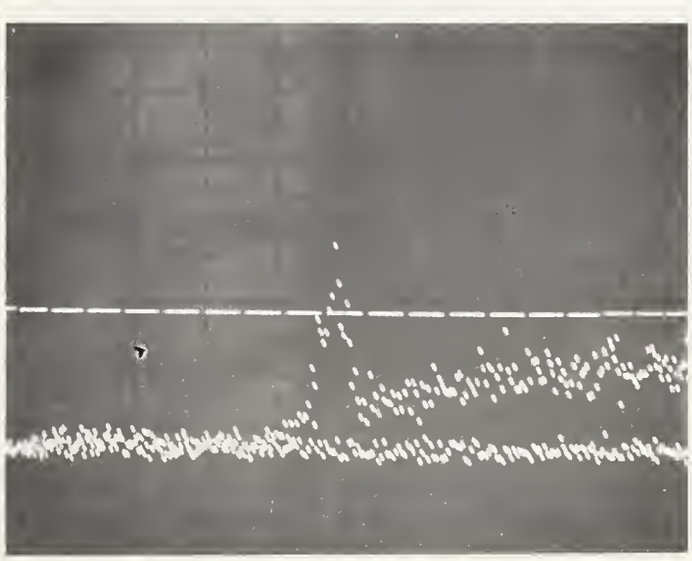
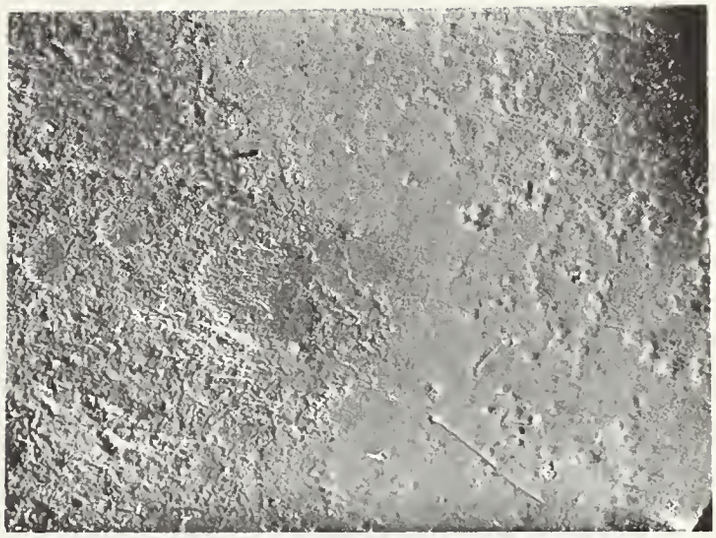


Figure 21 Target Current Plus MgK_α

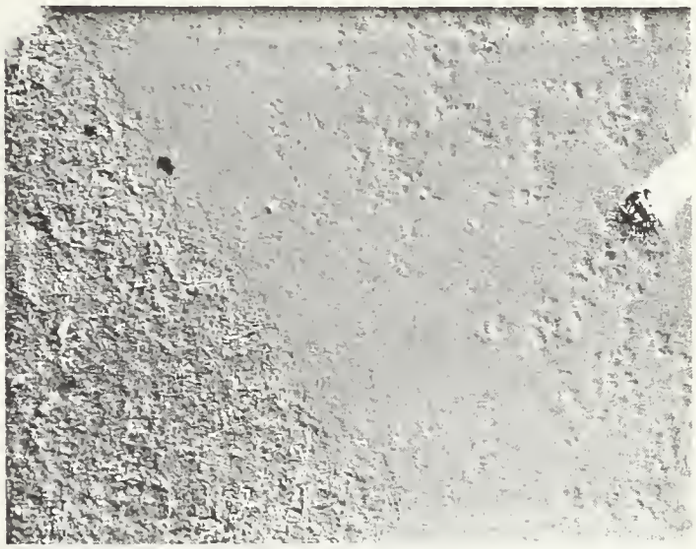
Aluminum



Ceramic

Figure 22.
Enameled 1100 Alloy
Not etched 4KX

Aluminum



Ceramic

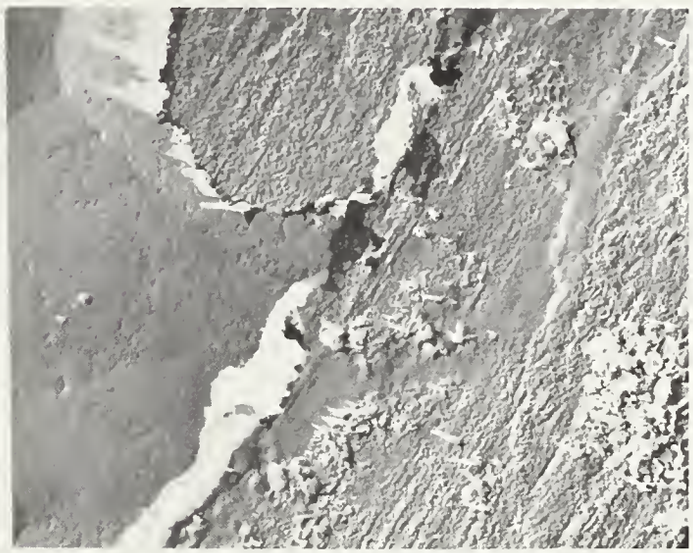
Figure 23
Enameled 1100 Alloy
Not etched 4KX

Aluminum

Ceramic

Figure 24.
Enameled 1100 Alloy
Etched 4KX

Aluminum



Ceramic

Figure 25.
Enameled 5154 Alloy
Etched 4KX

Figure 26. 625X
Alloy 1100 Chemical clean plus R-100
90 degree cross section

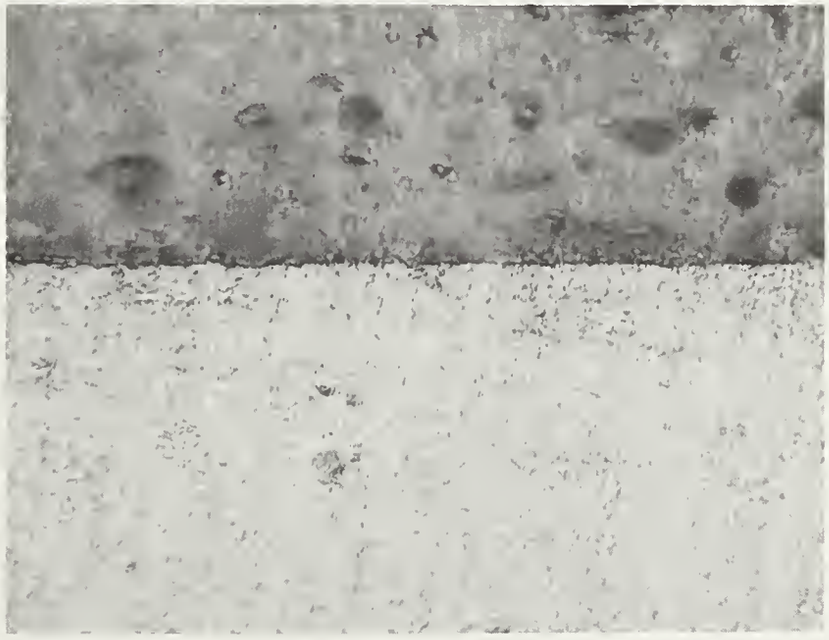


Figure 27. 625X
Alloy 6061 Chemical clean plus R-100
90 degree cross section


DEPARTMENT OF COMMERCE
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