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(Final Report)

INVESTIGATION OF RANDOM THICKNESS VARIATIONS IN CHEM-MILLED 2219-T37 ALUMINUM

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

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(Final Report)

Prepared by:

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April 29, 1965

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29745

ABSTRACT

A study has been made of random thickness variations in chem-milled, Type 2219-T37 aluminum alloy. A method was devised to simulate the production problem, employing a nonuniformly quenched bar specimen. In these specimens, the slower cooled zone is attacked more rapidly and develops a negligible amount of "smut" during chem-milling. The water-quenched zone is more slowly and nonuniformly milled, and develops a heavy and nonuniform-adherent smut. It is concluded that the slower attack is probably due to the shielding action of the smut deposit, and that the nonuniform attack results from the variations in smut retention.

Copper complexing additives (mostly amines) were screened for possible corrective action in the milling process; none was entirely satisfactory.

An approach to the problem is suggested in which a deliberately heavy and uniform smut is generated during milling, thereby inducing a uniform milling rate in spite of metallurgical variations. author

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INVESTIGATION OF RANDOM THICKNESS VARIATIONS IN CHEM-MILLED 2219-T37 ALUMINUM

I. INTRODUCTION

The technique of chemical milling is ideally suited to the fabrication of integrally-stiffened components of booster vehicles. The gore sections of tank bulkheads, for example, can be milled from precurved segments of full-strength aluminum alloy, thus avoiding the problems of heat-treating or cold-working such complex pieces.

Unfortunately, Type 2219-T37 aluminum--the alloy that has the best physical properties for such applications--sometimes shows nonuniform milling characteristics. This report presents the results of a study, the specific objective of which was the discovery of chemical milling solutions that would avoid nonuniform attack. A secondary goal was the clarification of the metallurgical and electrochemical causes of nonuniform metal dissolution.

The work was undertaken by NASA with the hope that it would assist manufacturers of chemically milled components in improving the quality of their products and reducing fabrication costs.

It should be pointed out at the outset that the entire field of chemical milling is highly proprietary. It is difficult, therefore, to study solution variations or chemical additions to the actual milling agents. Accordingly, the experimental work described below was carried out on simple solutions, based on sodium hydroxide, and containing additives selected for their possible effect in reducing the influence of metallurgical inhomogeneities in the metal.

II. DISCUSSION OF THE PROBLEM

A. The Chem-Milling Process

The term "Chem-Mill" is a trade name owned by North American Aviation, Inc., and licensed to Turco Products, Inc. Basically, the process includes two steps: (1) application of a "resist" coating to areas where no stock removal is desired, and (2) immersion of the work in a strongly alkaline solution for a sufficient time to mill the exposed regions to the required depth.

The application of the resist or "maskant" to the workpiece is accomplished by dipping, spraying, or brushing, and was not a subject in the present program.

B. Nonuniform Milling of Type 2219-T37 Aluminum

1. Production Experience

Chemical milling of pure aluminum can be carried out quite readily, with a very uniform removal rate over the surface of the work. Many of the fairly simple aluminum alloys can also be chemically milled with very satisfactory smoothness and uniformity.

When the same techniques are applied to the highly alloyed (and very high strength) Type 2219-T37 aluminum, however, certain thickness variations are observed in the milled areas. These take the form of ridges or "mesas" in an otherwise "flat-bottomed" region of stock removal. In general, these bumps or raised areas are equally smooth in finish to the deeper areas. Also, these areas of lesser attack are reasonably uniform in themselves. The average depth of attack, however, is very noticeably different from the remaining areas.

In order to overcome these difficulties, it has been necessary for fabricators of chemically milled components to employ a considerable amount of hand finishing on the nonuniform areas in order to meet required dimensional tolerances. Elimination of the need for such special work was the objective of this program.

2. Possible Causes

Because the difficulties just described were experienced with Type 2219-T37 alloy only, it was quite natural to deduce that some sort of compositional or structural inhomogeneity was responsible for the phenomenon. Furthermore, since the metallurgical processing of the alloy is essentially complete when the plate is delivered by the producer, it was also reasonable to conclude that the propensity for nonuniform milling was present in the material when so delivered.

Attempts had been made by the manufacturer to determine whether certain steps in the heat treatment process might be responsible for the nonuniform milling. In fact, tests of specially produced 2219-T37 plate indicated that certain laboratory-scale techniques did yield plate that showed very satisfactory milling characteristics. Extension of these special procedures to large-scale production of 2219-T37 plate did not, however, prove to be a satisfactory solution to the problem.

Specifically, it was thought that the very high copper content of Type 2219 aluminum alloy might make it abnormally sensitive to minor variations in the cooling rate experienced by different areas of the plate during quenching from the solution-treatment temperature. (See Table I for composition and processing of Type 2219-T37 alloy.) This theory was supported by studies of the microstructure(1, 2) carried out by two manufacturers of the alloy. A summary of these references follows.

Metallographic examination and comparison of structure of (1) "fast" milling, and (2) "slow" milling regions of samples of 2219-T37 alloy showed the following:

(a) The fast-milling areas developed a gray smut, while the slow-milling areas accumulated a thick, black smut.

(b) The fast-milling areas showed a dense grain boundary precipitate, whereas the slow-milling zones had no significant amount of precipitation.

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(1) ALCOA, Physical Metallurgy Division, Report 13-43633, October 16, 1963.

(2) Reynolds Metals Company, Letter of February 14, 1964, to W. Travis, reporting metallographic examination of 2219-T37 plate.

TABLE I

METALLURGICAL DATA FOR TYPE 2219-T37 ALUMINUM ALLOY

Analysis	%
Cu	5.8-6.8
Mn	0.20-0.40
Ti	0.02-0.10
V	0.05-0.15
Zr	0.10-0.25

Heat Treatment:
Solution treated at 985°-1005°F
Quenched in cold water (100°F, max)

Mechanical Treatment:
Stretched 7%

These data were interpreted to indicate that nonuniform quenching of the alloy plate was the probable cause of the metallurgical and chemical-milling variations.

During earlier studies of the problem it was also considered possible that nonuniform yielding during the 7% stretching treatment (Table I) might be responsible for the chemical milling difficulties.

III. PLAN OF RESEARCH

A. Objective

Whatever the basic cause of the nonuniform milling, this program was directed toward discovering chemical compositions that could produce uniform attack in spite of metallurgical aberrations in the alloy. In other words, even though the 2219-T37 condition is extremely delicate to produce, the physical properties attainable are sufficiently attractive to justify searching for more tolerant milling solutions.

B. Experimental Plan

A purely empirical approach to the study of candidate solutions was elected, guided by the reasonable hypothesis that the high copper content of the alloy was in some way related to the variations in milling rate.

Based on knowledge available at the beginning of the program, it appeared likely that minor variations in quenching rate from point to point on the specimen led to a corresponding variation in the amount (or form) of a copper-containing precipitate. This, in turn, led to nonuniform dissolution of the aluminum matrix--by a mechanism that was not entirely clear.

The basic ingredient of chemical-milling solutions for aluminum is sodium hydroxide, in which aluminum metal is rapidly and completely soluble. Copper, however, is relatively inert in alkali. It could, therefore, be expected to influence the milling rate of an alloy, depending on the size, shape, and distribution of copper-bearing particles in the aluminum matrix.

It is reasonable to assume that the addition of a copper-complexing chemical to the alkali might reduce the sensitivity of the milling rate to the condition of the copper. Such an experiment was performed under NASA auspices (Contract No. NAS8-11718, Straza Industries, September 4, 1964), using sodium cyanide as the copper complexing agent.

The results were encouraging, although handling and disposition of the cyanide required that certain safety precautions be taken. It was therefore considered worth while to investigate other copper complexing agents.

C. Selection of Metal Specimen

When the program was originally formulated, the survey of experimental milling solutions was to be made on samples of Type 2219-T37 alloy which were known to exhibit random thickness variation during milling. Accordingly, a statistical approach was planned, which would take into account the fact that a randomly selected specimen might or might not show variability in milling rate.

After typical examples of nonuniformly milled stock were examined, however, it became evident that it would be virtually impossible to develop meaningful data on experimental milling compositions unless a "synthetic" aluminum specimen could be devised--one which would reproduce or simulate the naturally occurring phenomenon.

Working on the hypothesis that nonuniform quenching was responsible for nonuniform milling, the following specimen preparation was adopted:

> Rectangular bars of Type 2219-T37 aluminum were sawed from 0.406 in. thick plate, 1/2 in. wide by 8 in. long. These were solution treated at 990°-1000°F and quenched in cold running water to a depth of 5 in.; the remaining 3 in. was cooled in air, partly by conduction and partly by convection.

Certain specimens were then pulled in a tensile testing machine until they had elongated 7%, thus simulating very closely the condition designated as T37. The specimens were all cut from a single plate of 2219-T37 alloy. The location of each bar was noted, using the marking scheme shown in Figure 1. Thus, specimen milling characteristics could be correlated with gross plate geometry, if trends requiring such analysis were noted.

D. Apparatus and Milling Technique

As pointed out earlier, the objective of the program was to evaluate chemical milling solutions for their ability to produce uniform stock removal. It was considered desirable, therefore, to use relatively small containers for the baths, since only a few bars would be milled in each test composition.

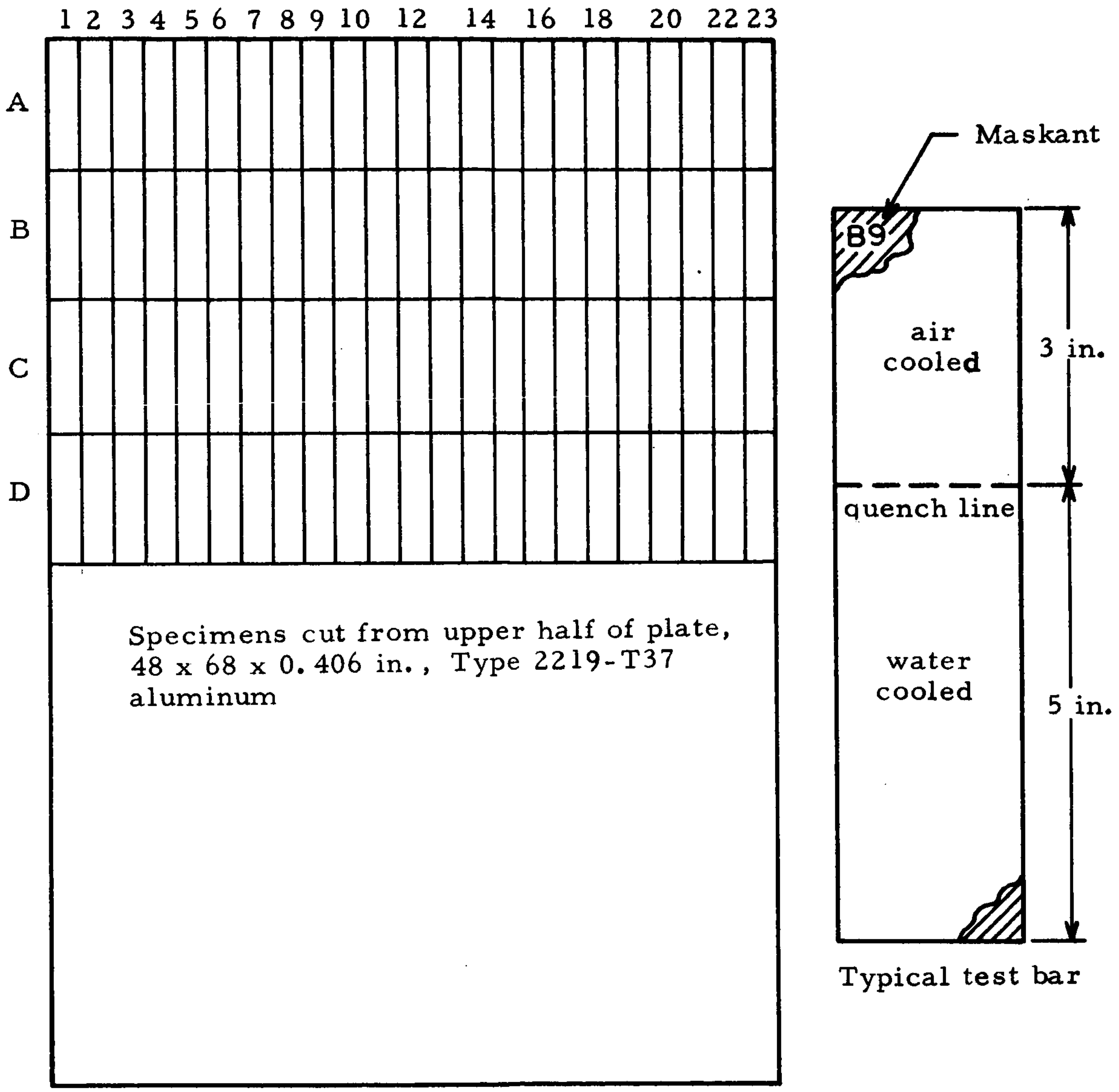
Accordingly, stainless steel tanks (of the type used for photographic work) were used as containers, heated by a water bath. The arrangement of tanks and the method of holding specimens is shown in Figure 2.

The base composition of the chemical milling solutions was 15 oz/gal NaOH. In some runs, the bath also contained 0.5 oz/gal of carboxymethyl cellulose (CMC). Additions of the various copper-complexing substances were made to one or the other of these basic compositions.

Periodic additions of NaOH were made to maintain the bath level between 14 and 16 oz/gal. These additions were based on the stoichiometric equivalence between the reactants, as represented by the equation:

$$\mathrm{Al}\ (27) + \mathrm{NaOH}\ (40) + H_2O \dashrightarrow \mathrm{NaAlO_2} + 3/2\ H_2$$

Thus, for every gram of aluminum dissolved, about 1.5 grams of NaOH were added.



Specimens cut from upper half of plate, 48 x 68 x 0.406 in., Type 2219-T37 aluminum

Typical test bar

FIG. 1 - METHOD OF CUTTING AND MARKING SPECIMENS.

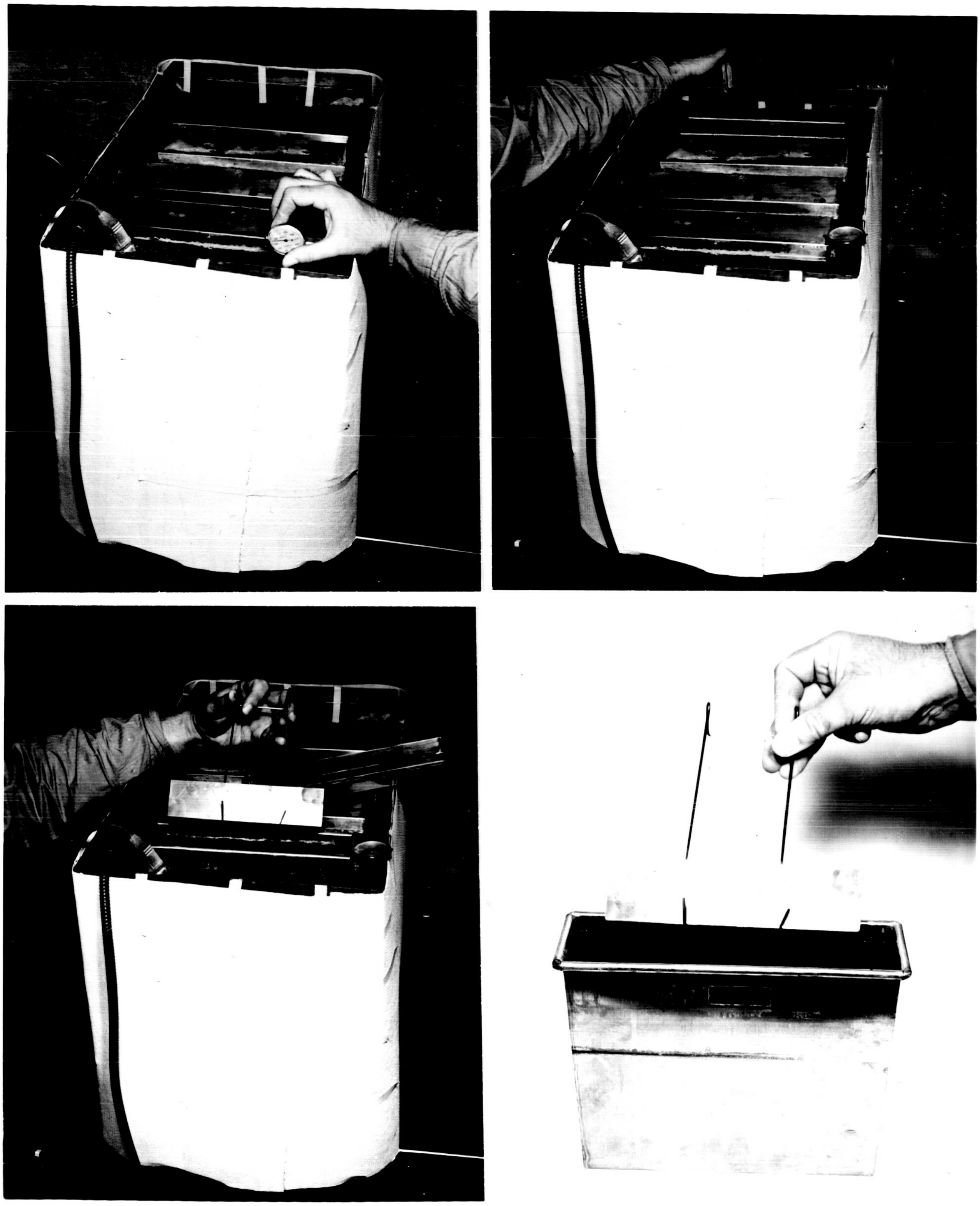


FIG. 2 - LABORATORY CHEMICAL MILLING APPARATUS.

Exact determination of the NaOH content of a bath was accomplished by titration with HCl, using direct measurement of pH to determine the equivalence point. The presence of sodium aluminate made the use of an indicator unsatisfactory. A typical curve for a spent bath is shown in Figure 3.

In general, exposure times for specimens were from 1 to 3 hr. Stock removal was from about 10% to about 50% of the original thickness, depending upon the temperature, time, and specific sodium hydroxide level of the solution for the particular run.

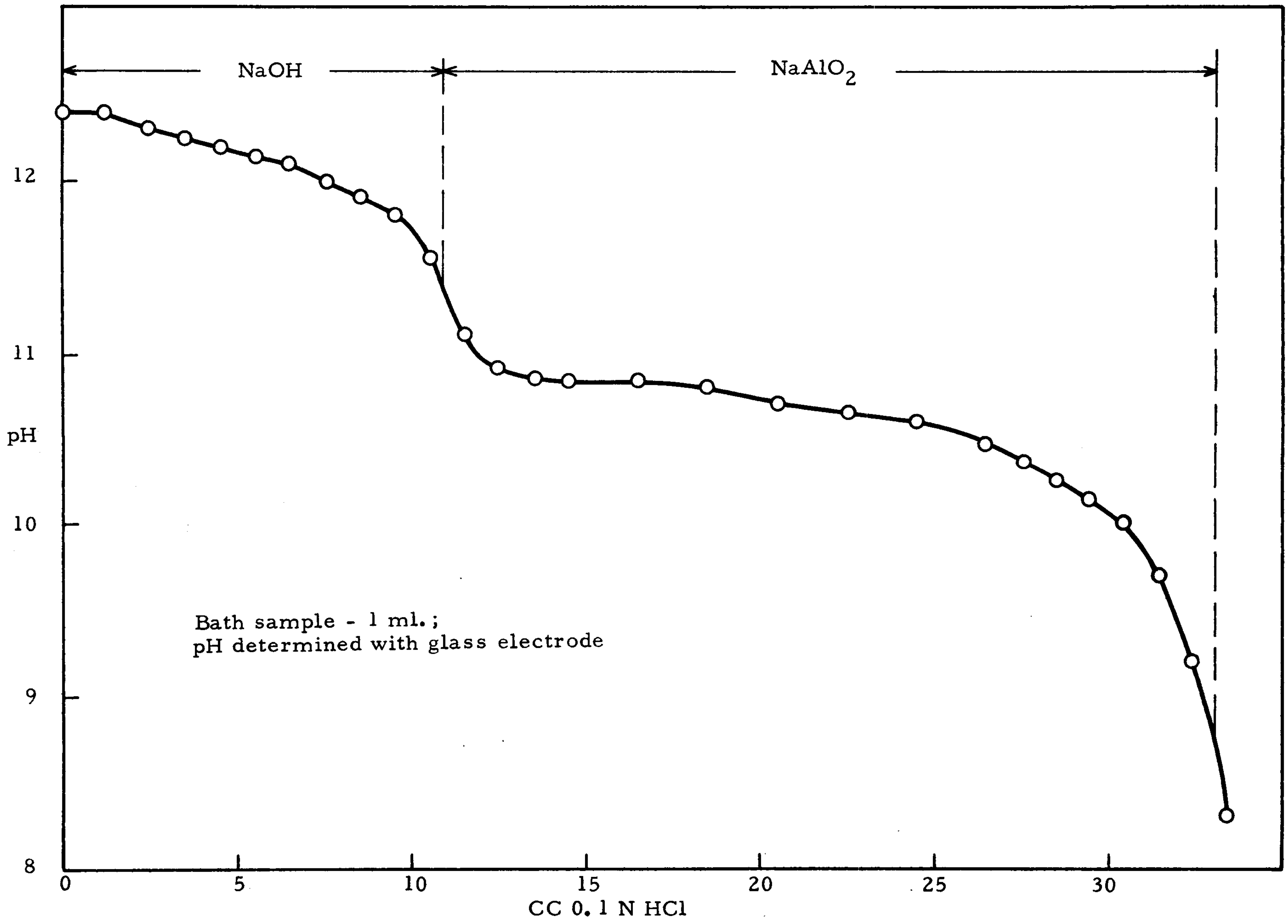
After milling, a specimen was removed from the bath, rinsed in running water, and "de-smutted" in approximately 30% nitric acid. Smut removal was rapid in regions where the coating was thin, but several minutes were required in heavily-coated regions.

IV. EXPERIMENTAL RESULTS

A. Preliminary Runs

A number of "nonuniformly quenched" test bars were chemically milled in sodium hydroxide solution, using the basic bath described above. The back side and edges were masked with Turcoform Mask No. 18. The opposite corners of the top surface were also masked, so that the identification number would be preserved during milling and a reference thickness would be available for determining depth of milling.

A technique was also worked out for preparing a surface profile of the test specimens. A dial gage mounted on a magnetic base was placed on a steel flat. The gage was located in such a way that the specimen to be measured could be moved step-wise past the measuring point, allowing rapid recording of the depth of attack. Thickness was noted every quarter inch along the bar; all measurements were made on the center line. The results of these preliminary experiments are shown in Figures 4-7. Two facts are immediately apparent:



Bath sample - 1 ml.;
pH determined with glass electrode

FIG. 3 - TYPICAL TITRATION CURVE FOR NaOH CHEMICAL MILLING BATH.

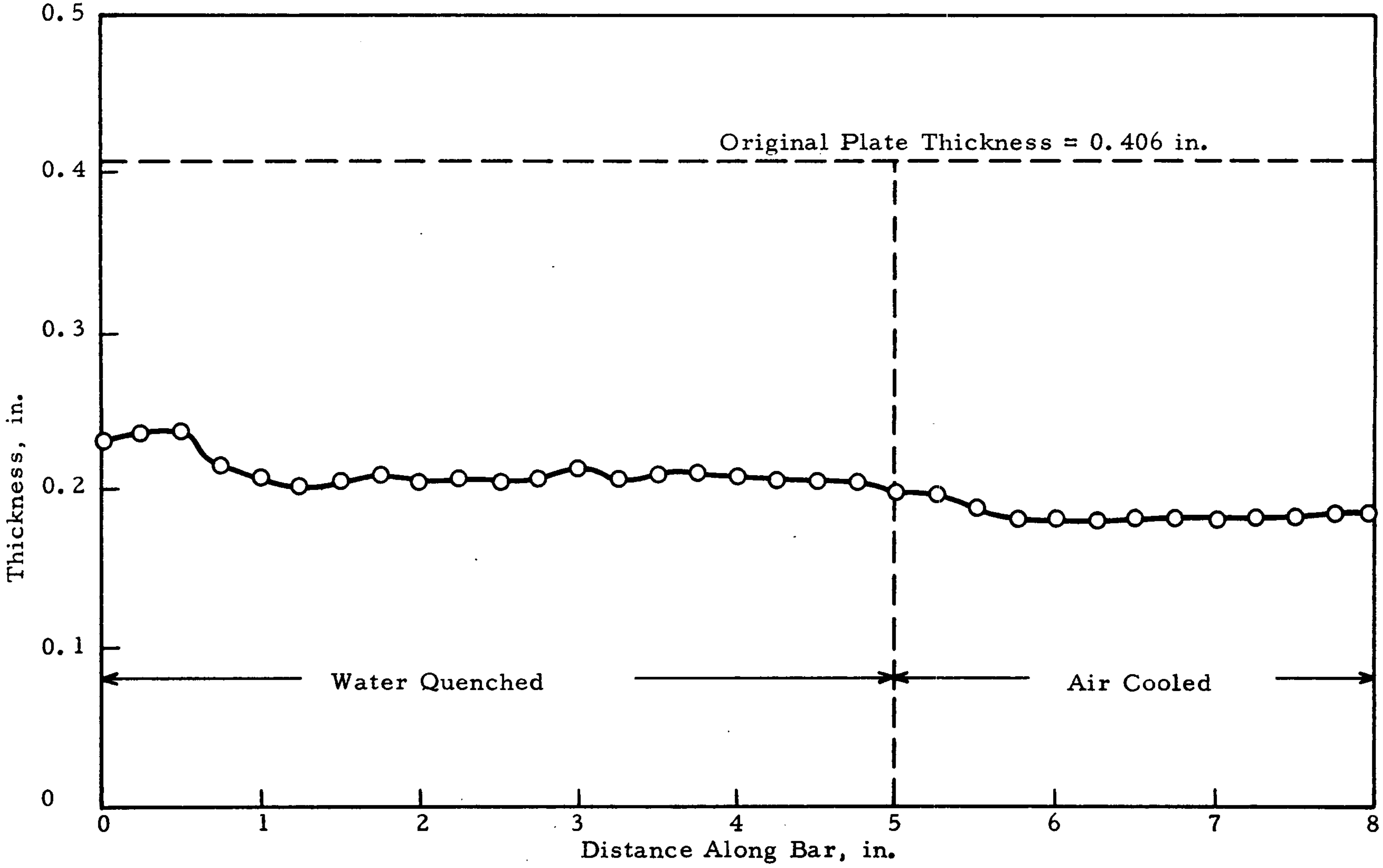


FIG. 4 - MILLING PROFILE FOR SPECIMEN B15 - NaOH

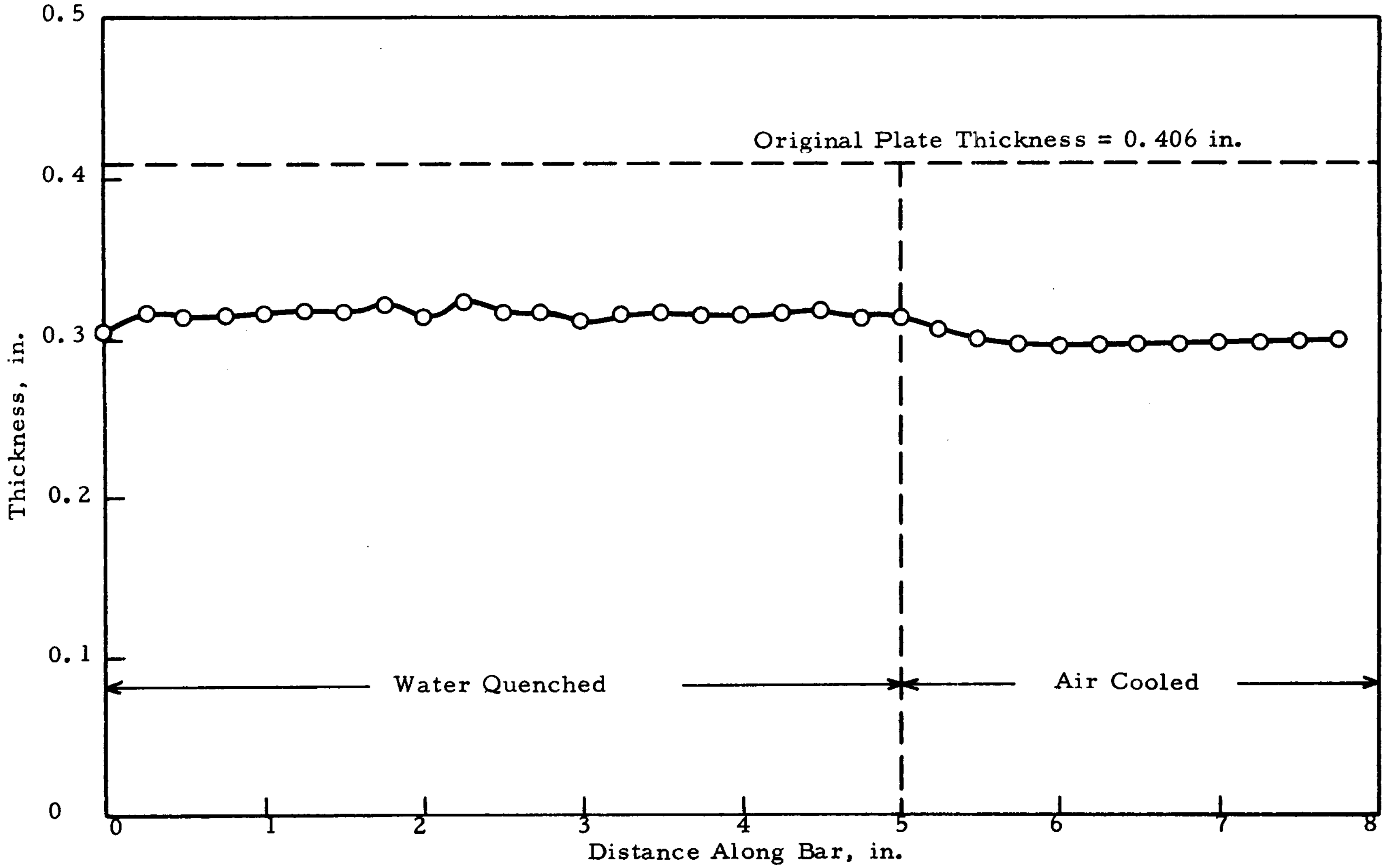


FIG. 5 - MILLING PROFILE FOR SPECIMEN A1 - NaOH

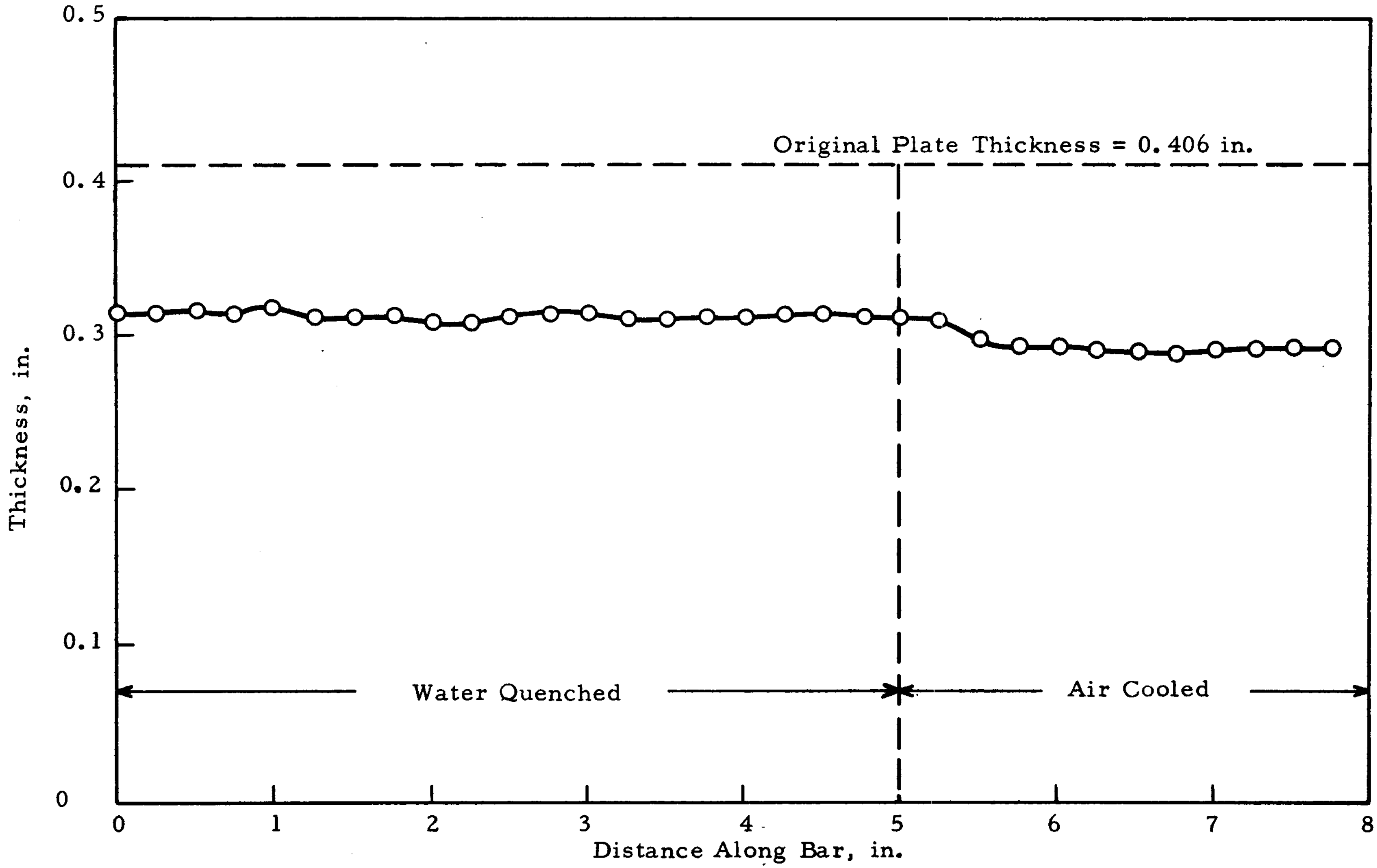


FIG. 6 - MILLING PROFILE FOR SPECIMEN A2 - NaOH

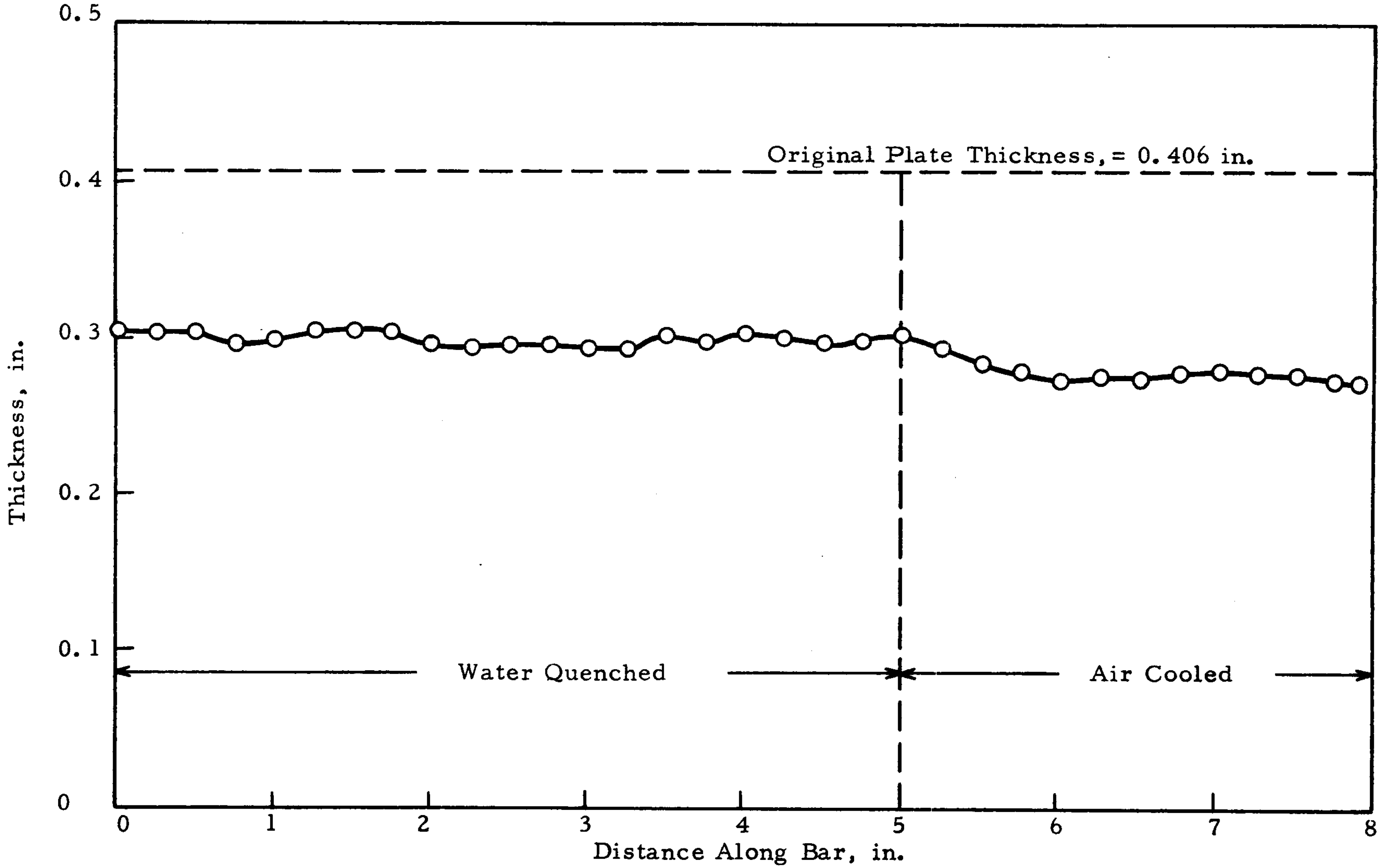


FIG. 7 - MILLING PROFILE FOR SPECIMEN A3 - NaOH

1. The greater degree of attack occurs in the air-cooled zone in every case.
2. The uniformity of attack is much better in the air-cooled region than in the water-quenched area.

It was also noted that the smut was removed in a few seconds from the air-cooled end of the bar, whereas the (much thicker) smut on the water-quenched end required several minutes to dissolve completely.

Closer simulation of the T37 temper in a nonuniformly quenched specimen was tried next. Specimens prepared as described above were pulled in a tensile test machine until the total elongation was about 7%. They were masked and chemically milled in the standard manner. The results are shown in Figures 8-10.

The presence of cold work in the bars did not appear to alter the character of the caustic attack on the air-cooled end; the nonuniformity of attack in the water-quenched end is quite evident however (Figure 10), and the difference in rate of stock removal between the air-cooled and water-quenched zones is also marked (Figure 9).

At this point, the effect of carboxymethyl cellulose was studied briefly. Figures 11 and 12 show the milling profiles for samples run in a bath with and without 0.5 oz/gal of CMC. No significant difference was noted; most further experiments were run in a simple alkali bath.

B. Electrochemical Effects

Before beginning the study of copper-complexing additives, it was decided to investigate the effect of applied current on the milling phenomenon. This approach was based on the following reasoning:

1. In the preliminary runs just described, the smut which formed on the specimen appeared to be high in metallic copper. Although the smut was very black when the specimen was removed from the alkali, it developed a copper color during exposure to nitric acid.

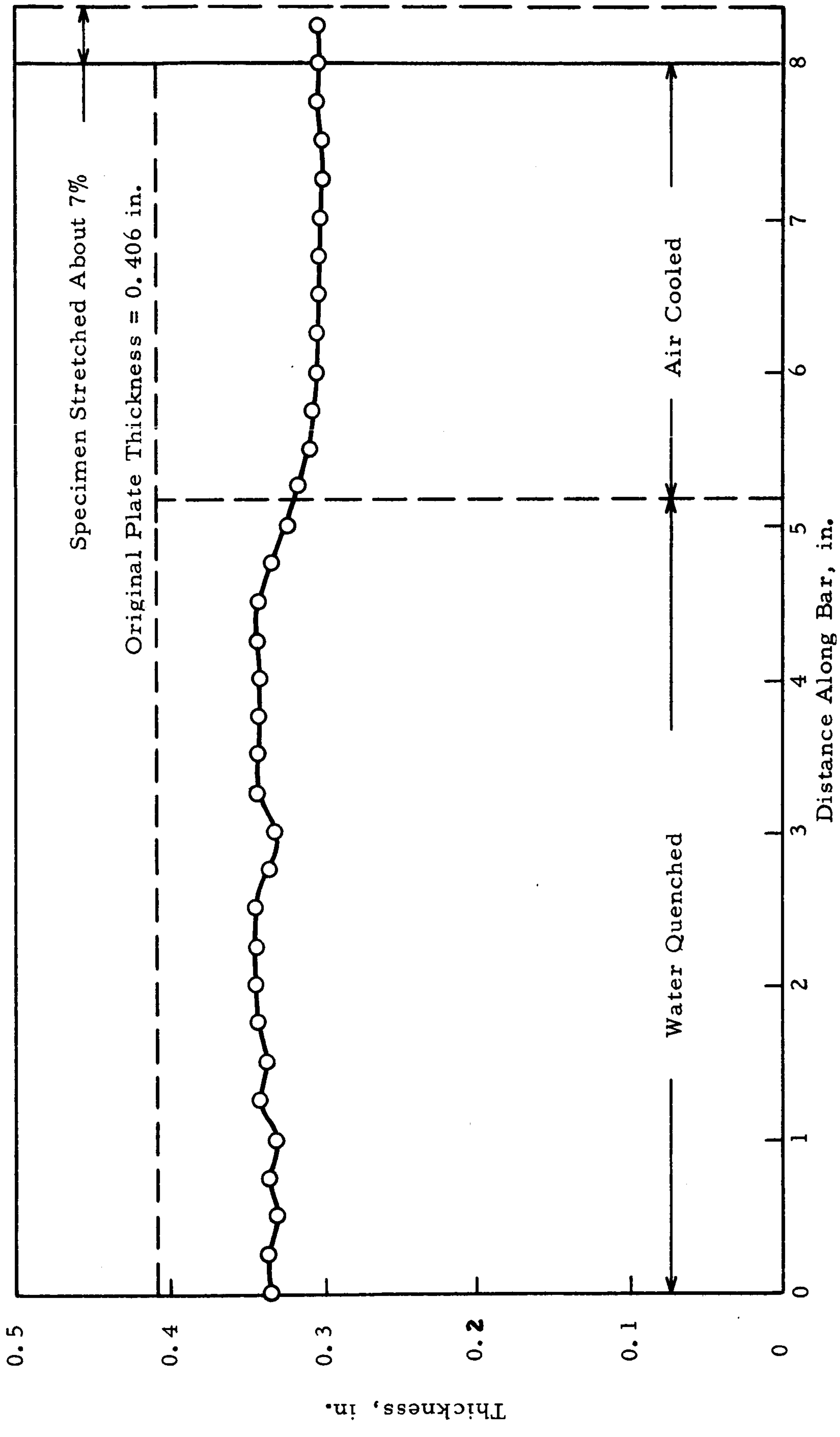


FIG. 8 - MILLING PROFILE FOR SPECIMEN C9 - STRETCHED 7%

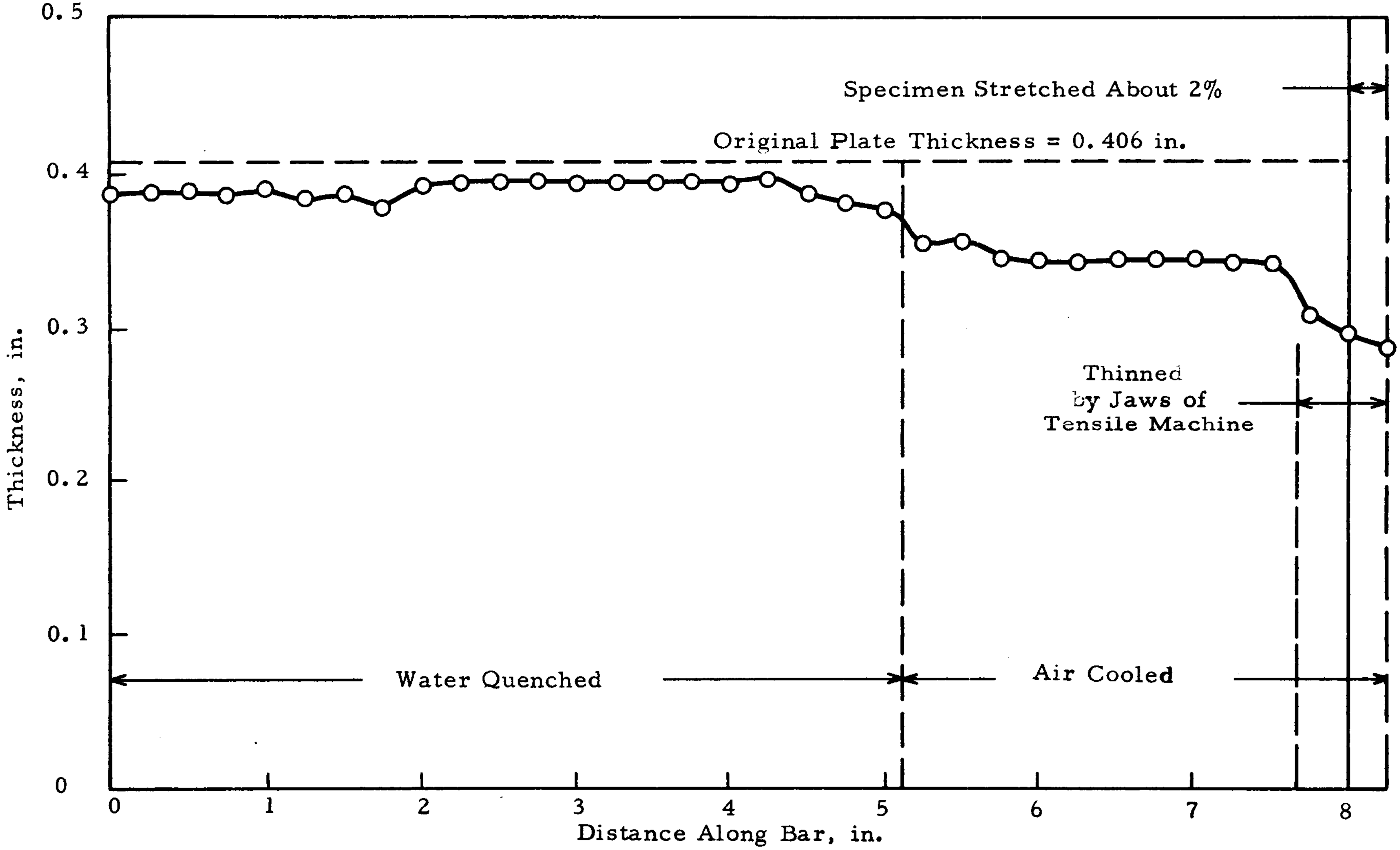


FIG. 9 - MILLING PROFILE FOR SPECIMEN C8 - STRETCHED 2%

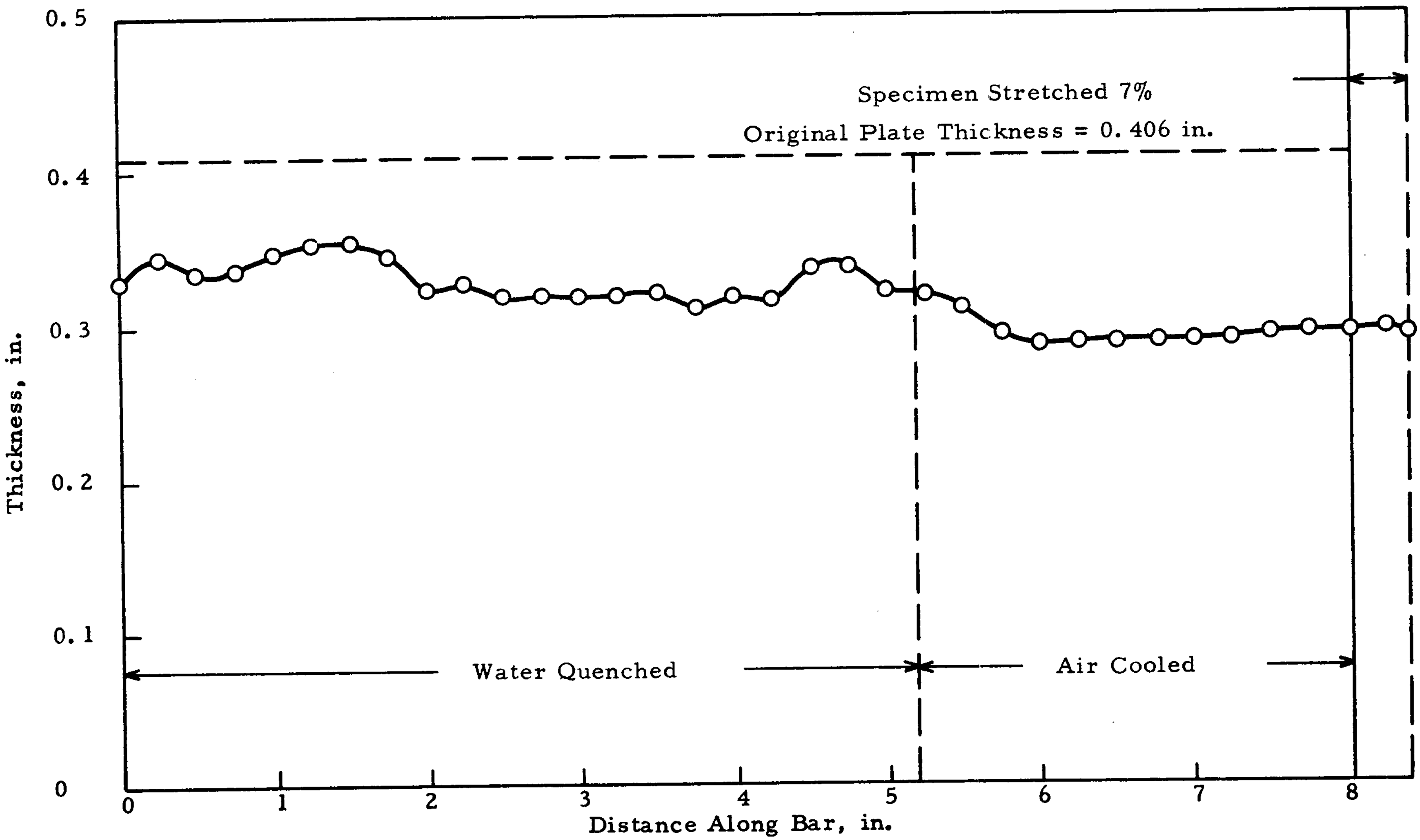


FIG. 10 - MILLING PROFILE FOR SPECIMEN A9 - STRETCHED 7%

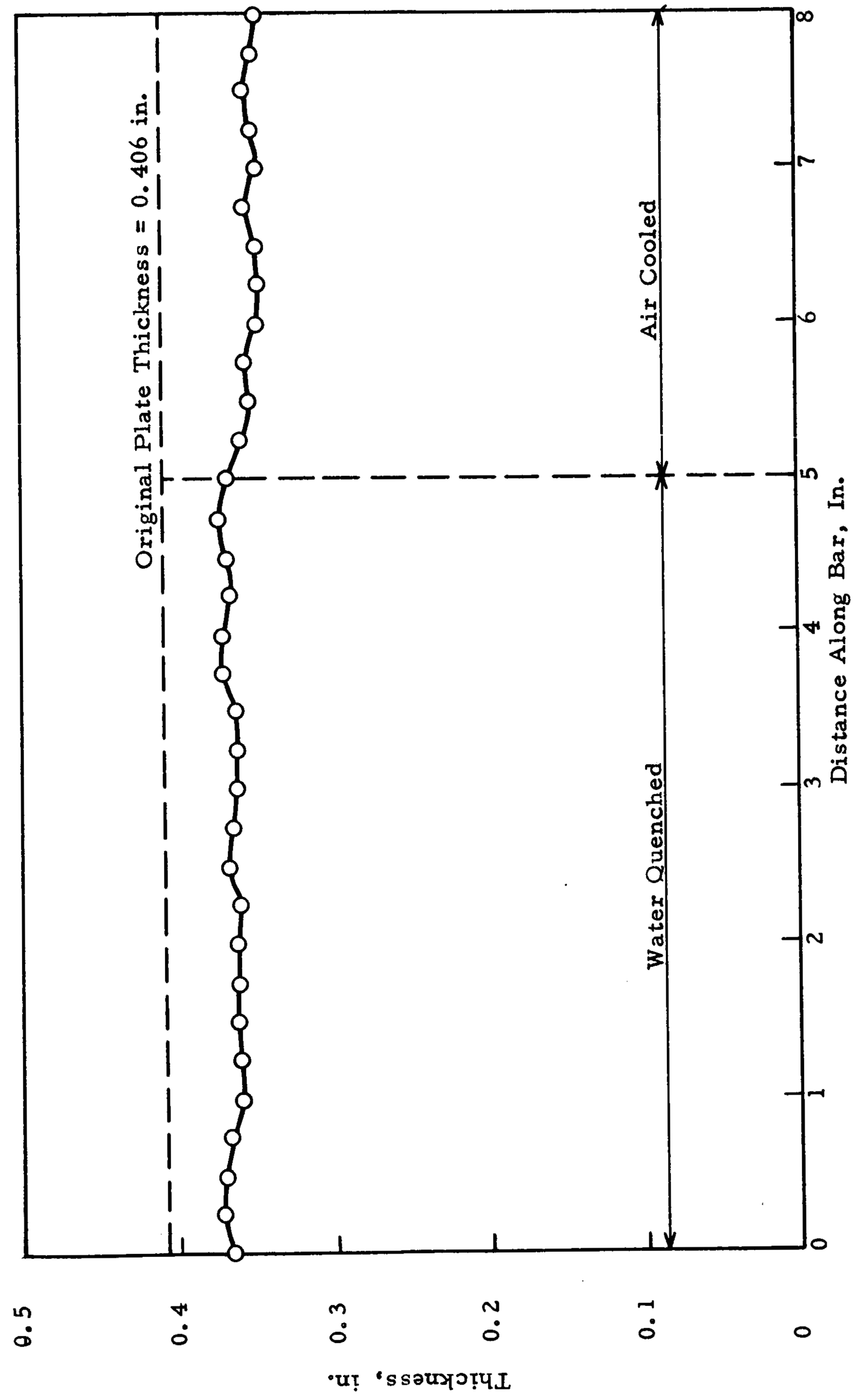


FIG. 11 - MILLING PROFILE FOR SPECIMEN A5 - CMC

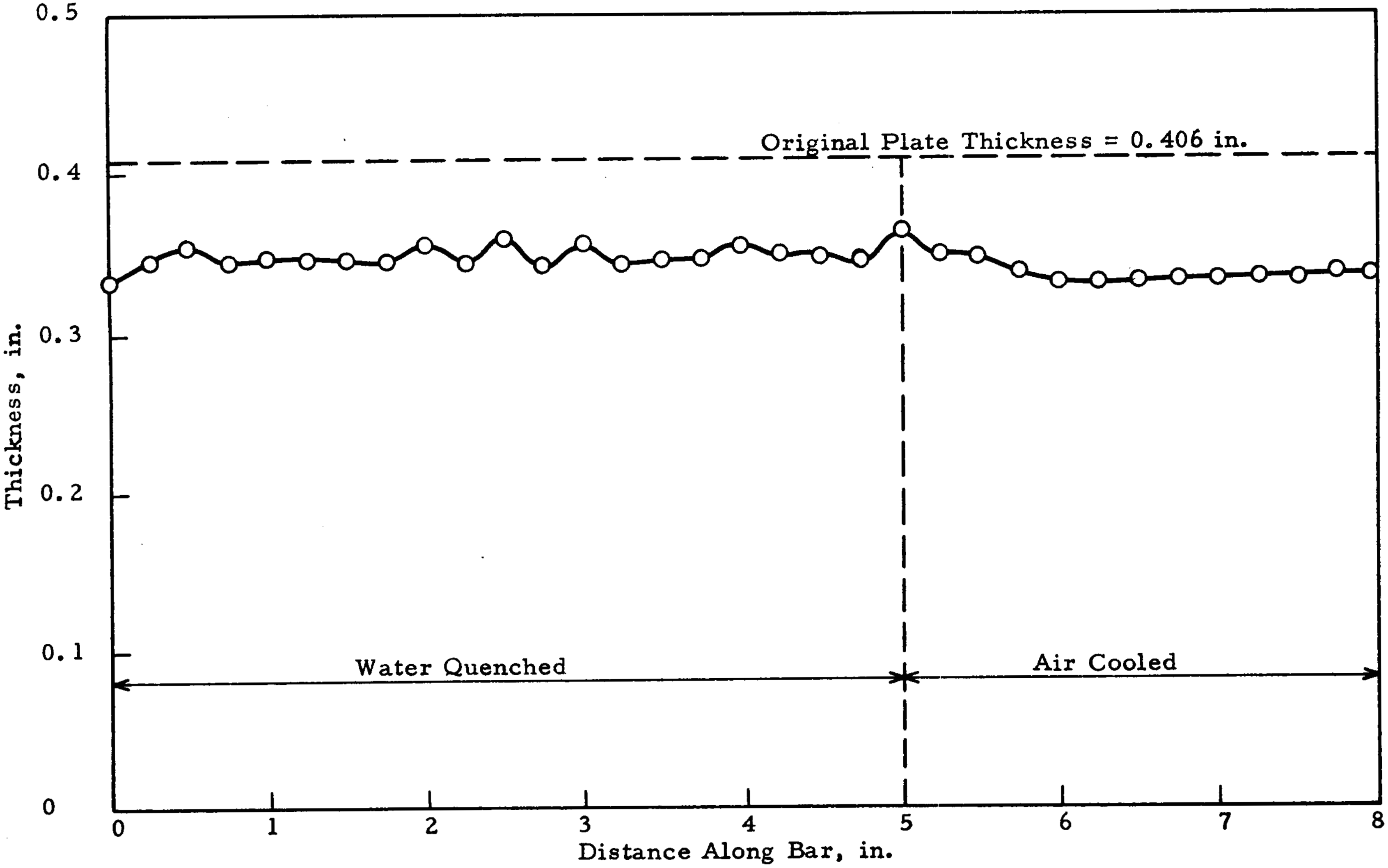


FIG. 12 - MILLING PROFILE FOR SPECIMEN A6 - CMC

2. On the other hand, the long time required to dissolve the heavy smut indicated that it was not copper alone (which dissolves extremely rapidly in HNO_3), but probably contained a large proportion of iron and perhaps other elements (including aluminum as $CuAl_2$).

3. If copper and iron were being deposited on the specimen surface by a process of "cementation" or "immersion plating," it might be possible to prevent such redeposition by application of an anodic current.

Accordingly, a number of electrochemical experiments were performed, with the objective of learning more about the mechanism of smut formation.

1. Coupling to Copper Screen

A standard quenched (but unstretched) test bar was fitted with a piece of copper screen, arranged to cover the exposed face of the bar. The back was masked, and the copper was bent in such a way that it contacted the aluminum at the edges of the bar.

After exposure to the milling bath for 120 min, the bar was removed and examined. The degree of attack was reduced to about 20% of normal, in spite of the couple action provided by the copper. (One might reasonably expect the copper-aluminum couple to undergo accelerated attack.)

2. Applied Current

These results prompted a series of experiments in which current was applied to an aluminum specimen during milling, using an external source of either anodic or cathodic current. The stainless steel tank served as the second electrode, the specimen being suspended centrally in the bath. Both stretched and unstretched samples were studied; no difference was noted in their response to applied current. The results are given in Table II.

TABLE II

EFFECT OF APPLIED CURRENT ON MILLING RATE

Specimen	Stretched	Applied Current, amps	Time, min	Weight Loss, gm
B1	No	None	75	45
A19	Yes	None	75	58
A16	No	10 (cathodic)	75	27
A11	Yes	10 (cathodic)	75	26
B2	No	1 (anodic)	75	23
A20	Yes	1 (anodic)	75	27
A17	No	5 (anodic)	75	33
A18	Yes	5 (anodic)	75	33
A15	No	10 (anodic)	55	12
A12	Yes	10 (anodic)	55	12

Bath: NaOH 16 oz/gal

Temperature: 190°-200°F

It is evident that applied current--either anodic or cathodic--lowers the rate of metal removal. Furthermore, the application of current did not improve the uniformity of milling, as illustrated by Figures 13 and 14 selected from Table II.

In view of the large effect of couple action on the milling rate, a check was run on the effect of coupling to the stainless steel tank itself. The results are shown in Figures 15 and 16; no effect whatever was produced by insulating the specimen from the tank.

3. Potential Measurements During Milling

It is appropriate at this point to discuss measurements of the potential exhibited by aluminum specimens during chemical milling, although these experiments were actually performed after the chemical studies described below.

A reference electrode was constructed for use in the hot alkali milling bath. It consisted of a stainless steel tube, closed at the bottom end, and provided with a side opening about 4 in. from the bottom. The closed end was packed with mercuric oxide. Thus, an HgO reference half-cell was formed with adequate stability for use in hot NaOH solution.

Time-potential curves were determined, using a conventional recording potentiometer. Data were recorded for both water-quenched and air-cooled Type 2219 alloy and for Type 1100 aluminum. Curves were prepared for both NaOH (15 oz/gal) and for Turco 13B solution, as shown in Figure 17.

Several points may be noted concerning the time-potential curves:

1. The curves for NaOH are much more anodic than for the Turco solution.
2. The curves for Type 1100 aluminum are considerably more anodic than for Type 2219 alloy.
3. The curves for Type 1100 aluminum flatten very quickly after immersion. No smut formed on this alloy in either milling solution.

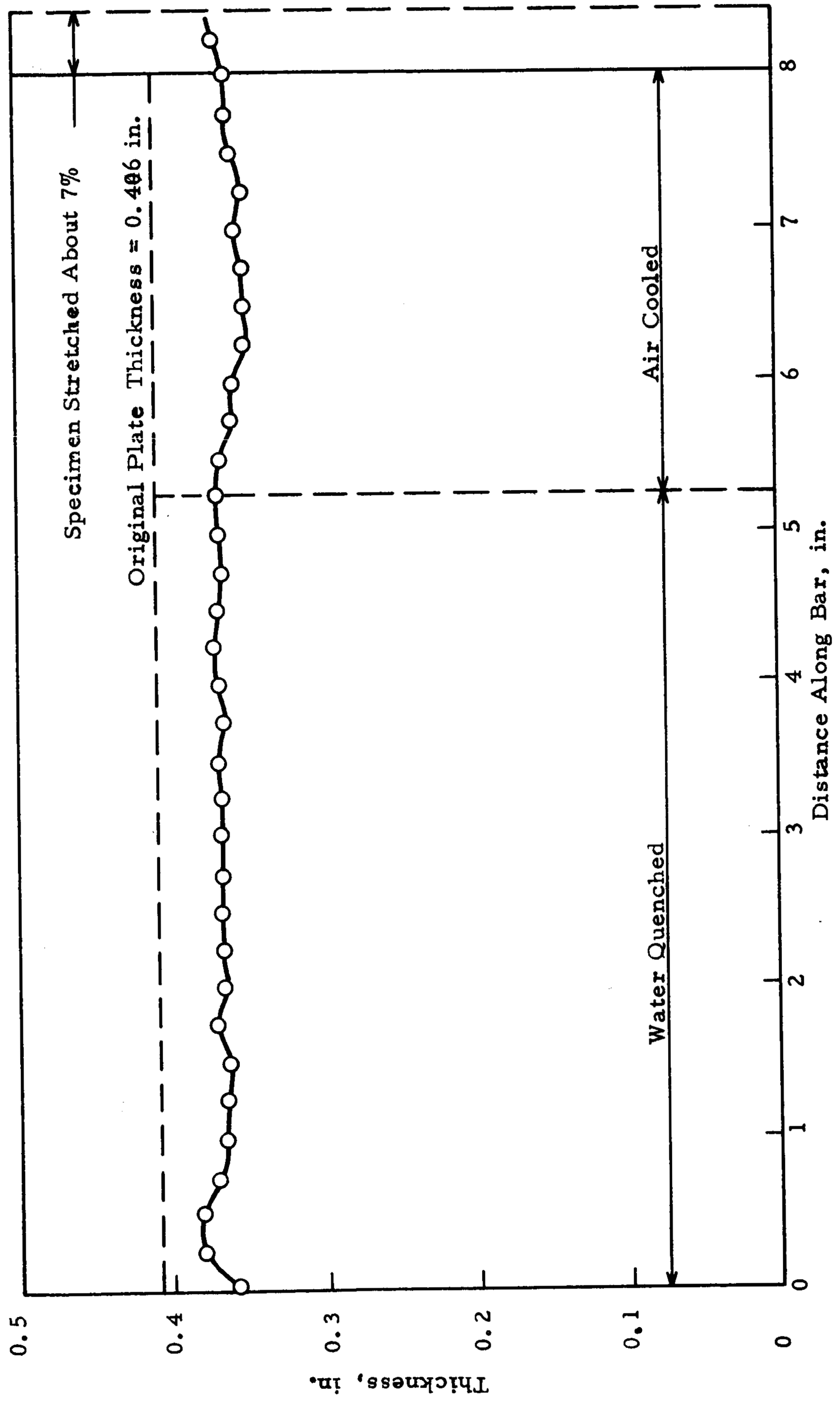


FIG. 13 - MILLING PROFILE FOR SPECIMEN A11 - CATHODIC CURRENT, 10 AMPS

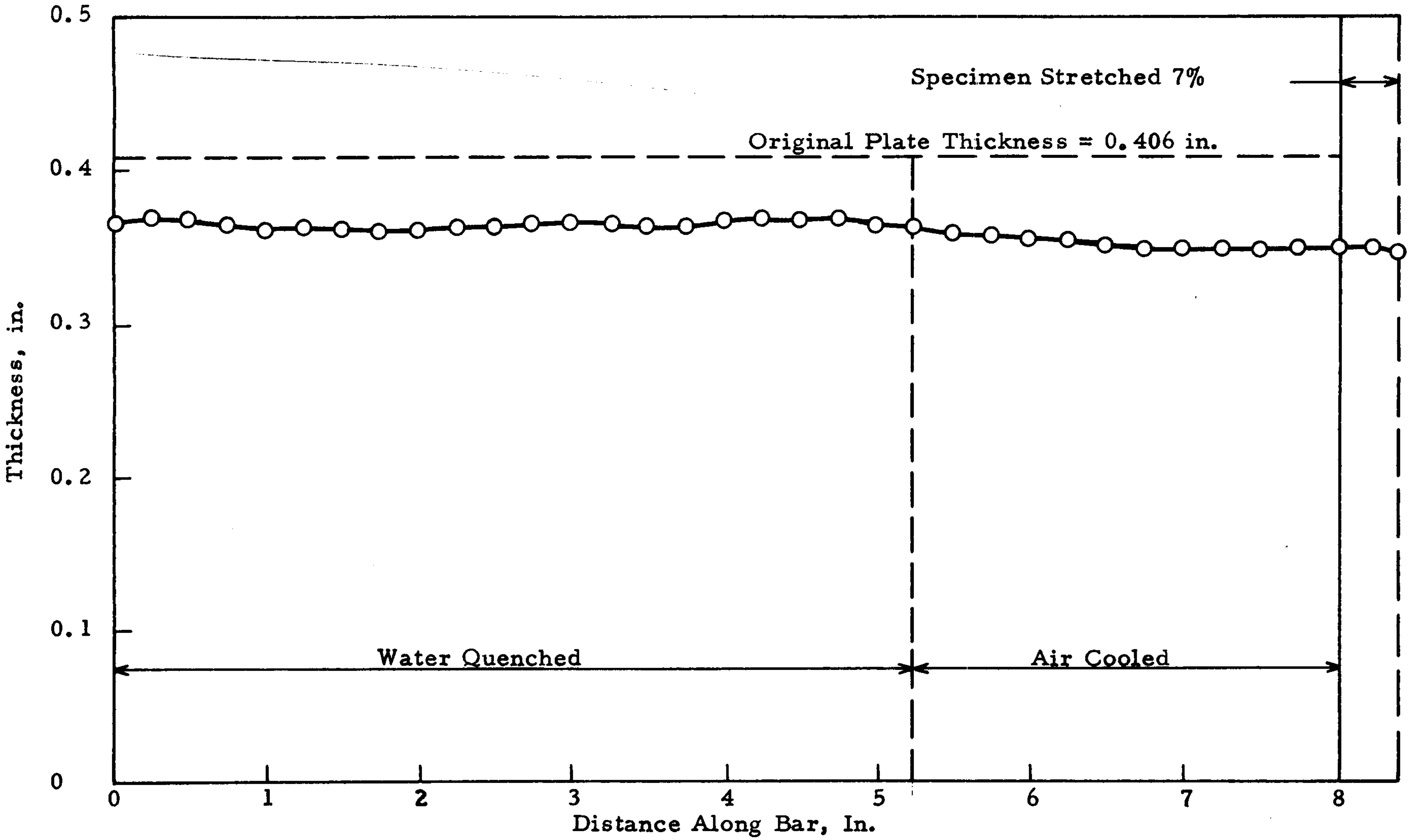


FIG. 14 - MILLING PROFILE FOR SPECIMEN A18 - CATHODIC CURRENT, 5 AMPS

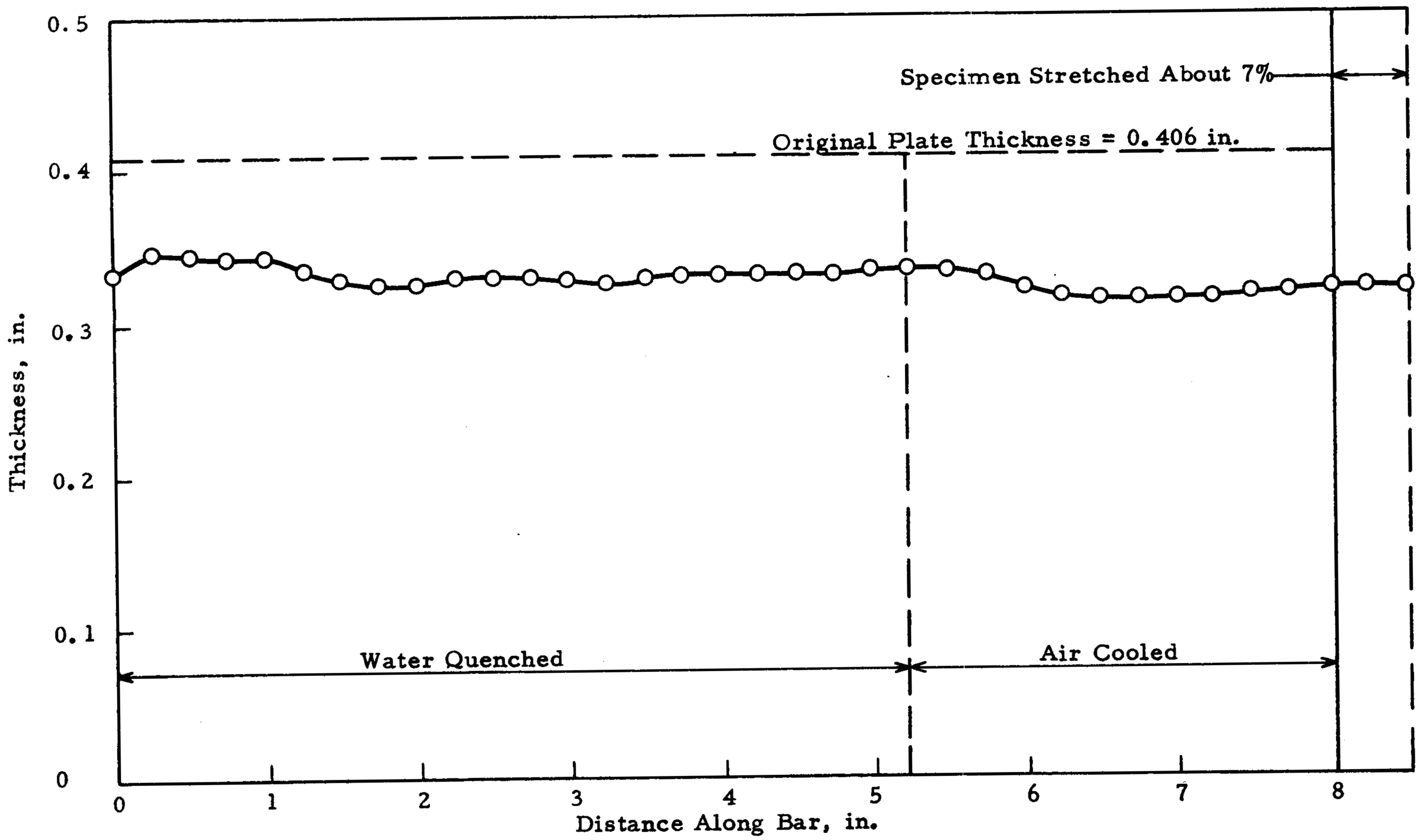


FIG. 15 - MILLING PROFILE FOR SPECIMEN A21 - INSULATED FROM TANK.

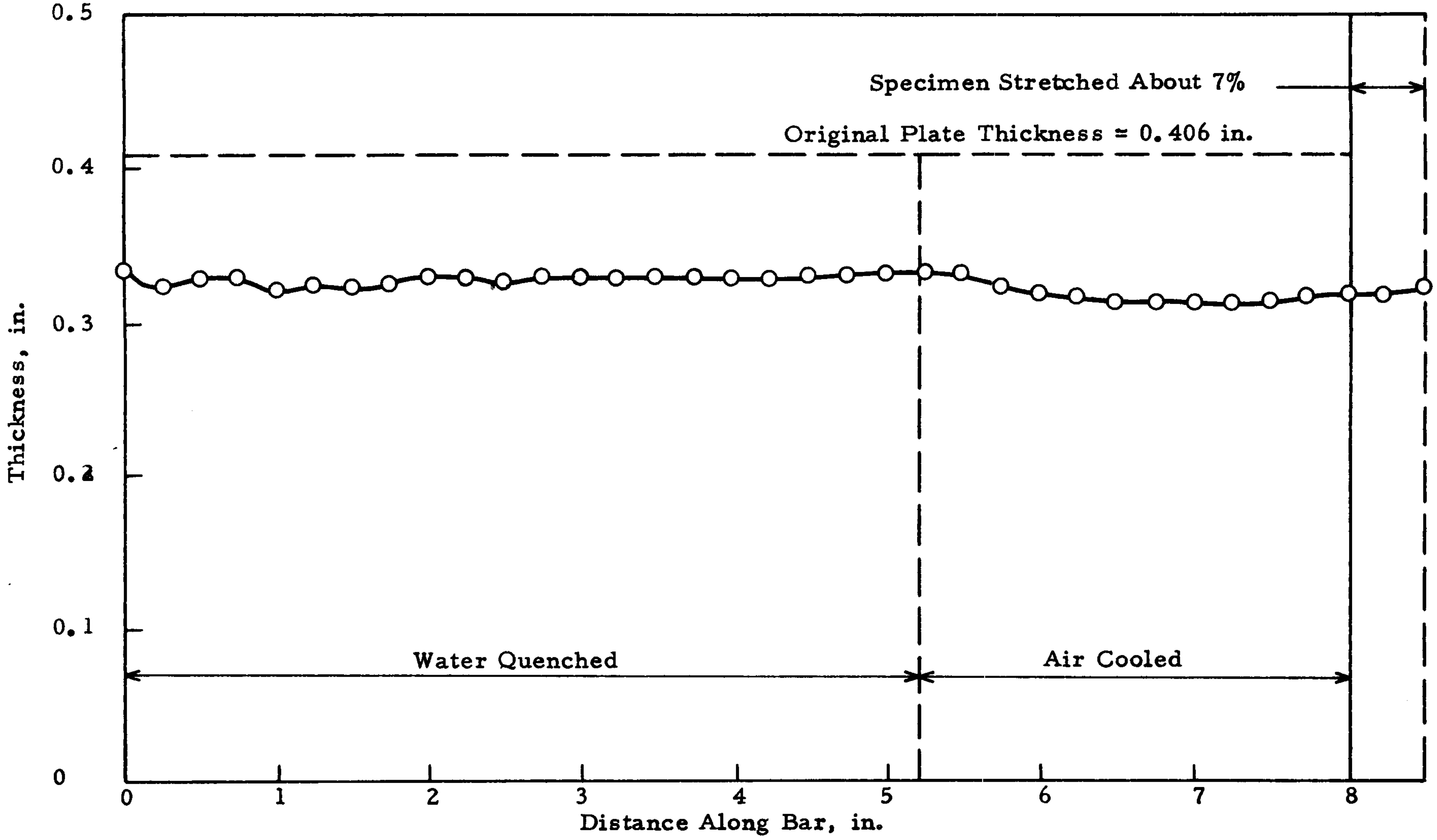


FIG. 16 - MILLING PROFILE FOR SPECIMEN A22 - NOT INSULATED FROM TANK

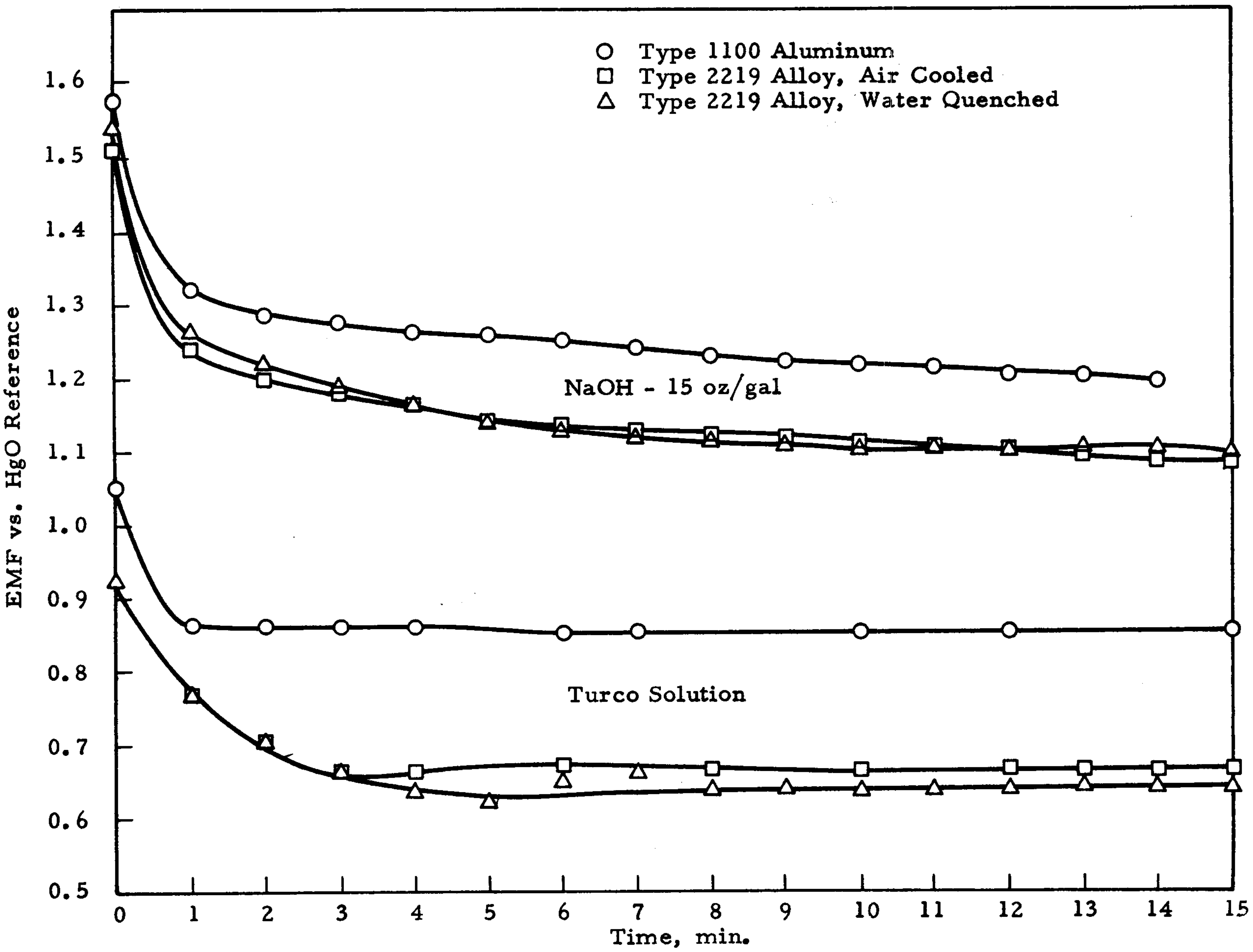


FIG. 17 - POTENTIAL-TIME CURVES DURING CHEMICAL MILLING

4. The curves for water-quenched and air-cooled Type 2219 are very close in both media. It is uncertain if a real difference exists, but there is some indication that the air-cooled alloy is slightly more anodic (more active).
5. The curves are all flatter in the Turco solution than in the NaOH.

All of these observations will be discussed in a later section.

C. Chemical Additions

A number of chemical substances were added to the basic milling solution. These were selected mostly for their possible complexing action with copper. The first, sodium nitrate, was included because it is an oxidizing agent and might, therefore, influence the electrochemical cell action in a favorable way by stimulating anodic action (through its depolarizing action at the cathodic sites).

In general, the level of each additive was the saturation value for the temperature used in milling (190°-200°F). The several chemicals used are shown in Table III, and the results of the milling experiments are shown in Figures 18-23.

The only additive which appeared to have a definite beneficial effect on the elimination of the nonuniform attack was tetraethylene pentamine. All the others had little or no effect; some even seemed to intensify the tendency toward step formation.

D. Smut Characteristics

1. Adhesion

The most striking feature of the chemical-milling process in NaOH solution is the remarkable difference in the nature of the smut formed on water-quenched vs. air-cooled zones. In no case did an adherent or heavy smut form on the air-cooled end of a specimen. On the water-quenched end, however, the smut frequently adhered completely. That is, there was left on the specimen a skeleton of residual material,

TABLE III

ADDITIVES TO CHEMICAL MILLING SOLUTION

Compound	Concentration, oz/gal	Profile Shown in Figure	Remarks
(1) Sodium Nitrate	5	18	Reduced rate of attack
(2) Ethylene diamine tetra acetic acid (sodium salt)	2	19	Definite step
(3) 8 - oxyquinoline	0.6	20	Definite step
(4) p - phenylene diamine	0.6	21	Definite step
(5) Tetraethylene pentamine	14	22	Some improvement
(6) 1,6 - hexanediamine	12	23	Bad step

Base Solution: 15 oz/gal NaOH

Temperature of bath: 190°-200°F

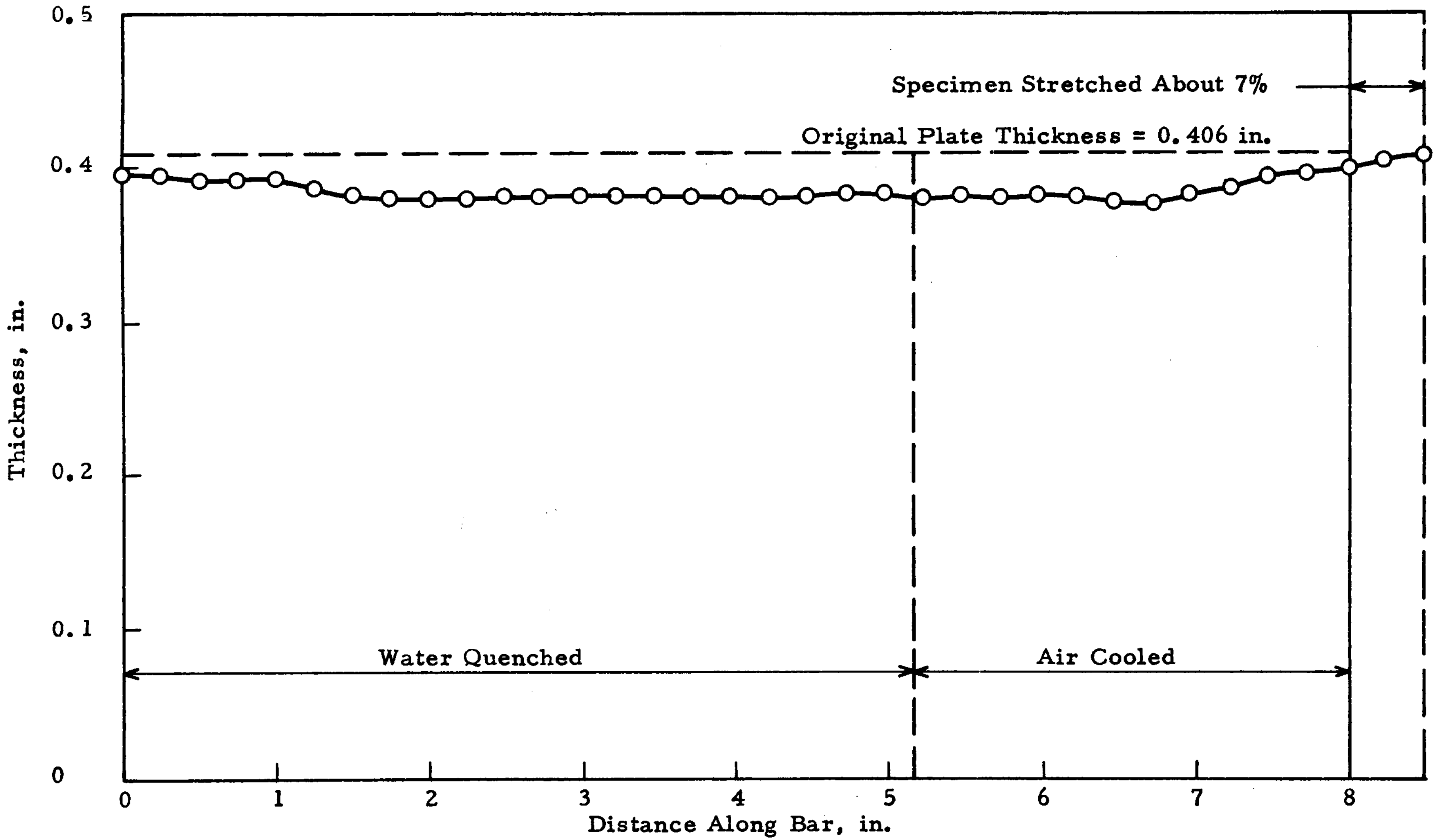


FIG. 18 - MILLING PROFILE FOR SPECIMEN B7 - SODIUM NITRATE

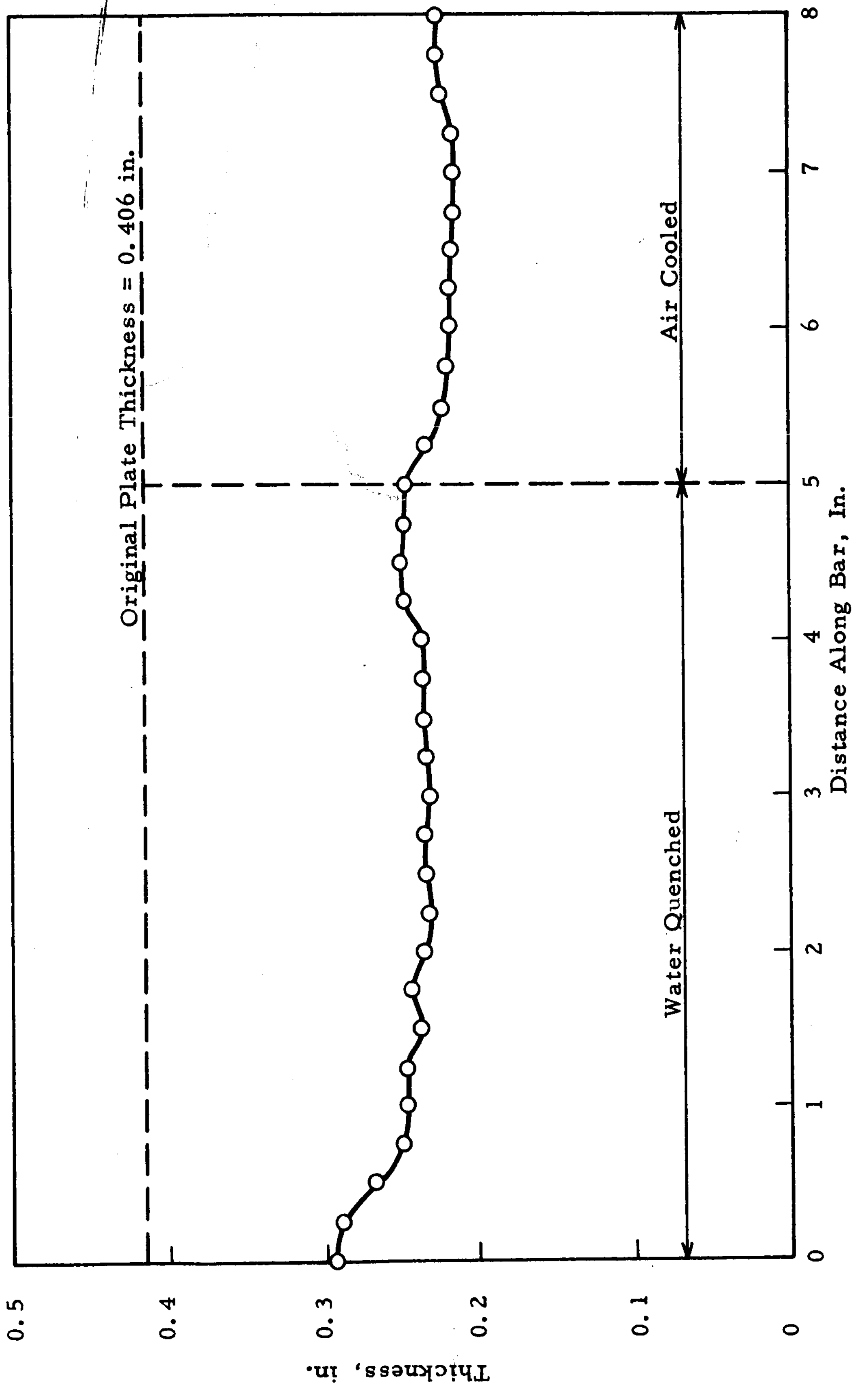


FIG. 19 - MILLING PROFILE FOR SPECIMEN C18 - EDTA

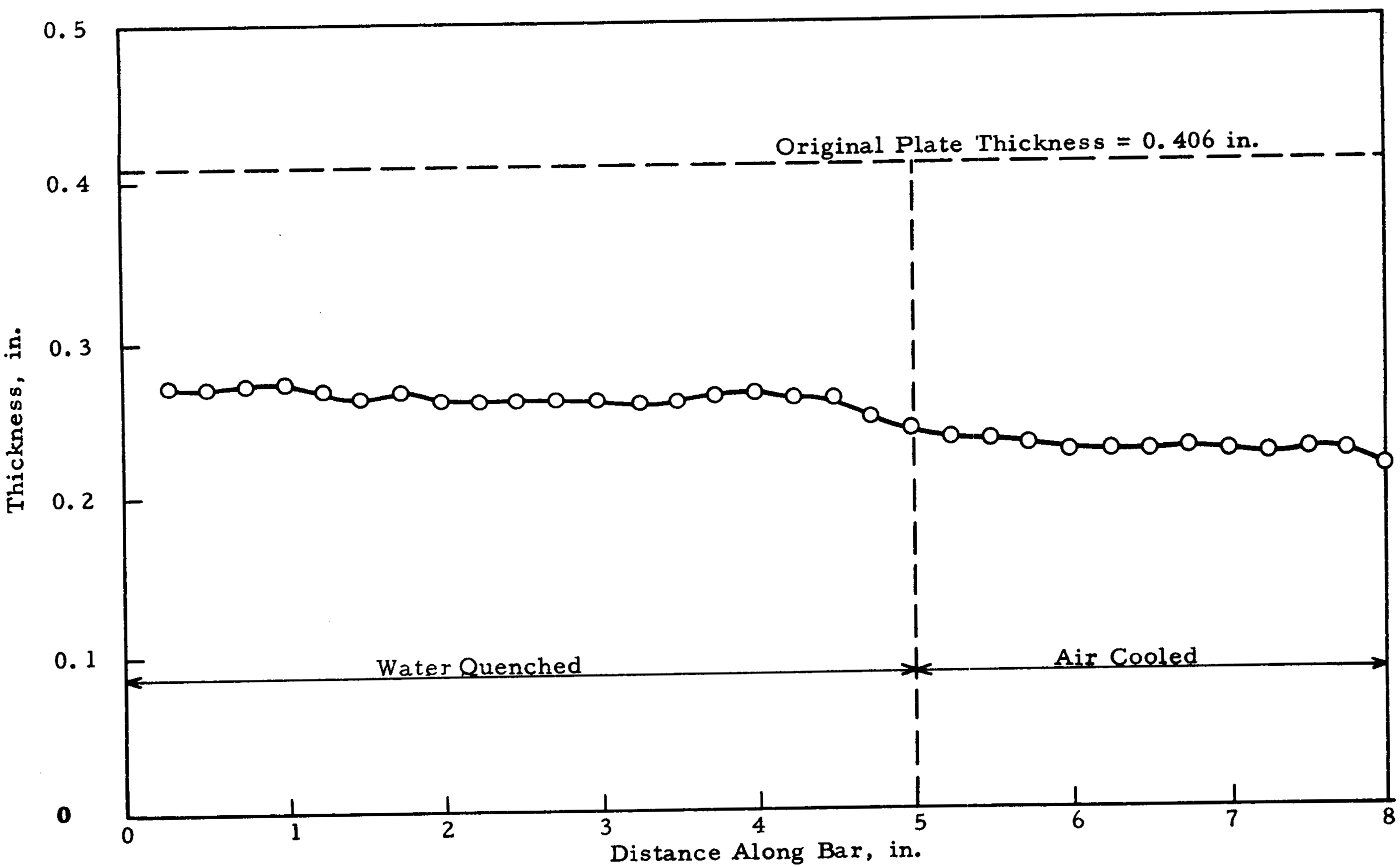


FIG. 20 - MILLING PROFILE FOR SPECIMEN C3 - 8 OXYQUINOLINE

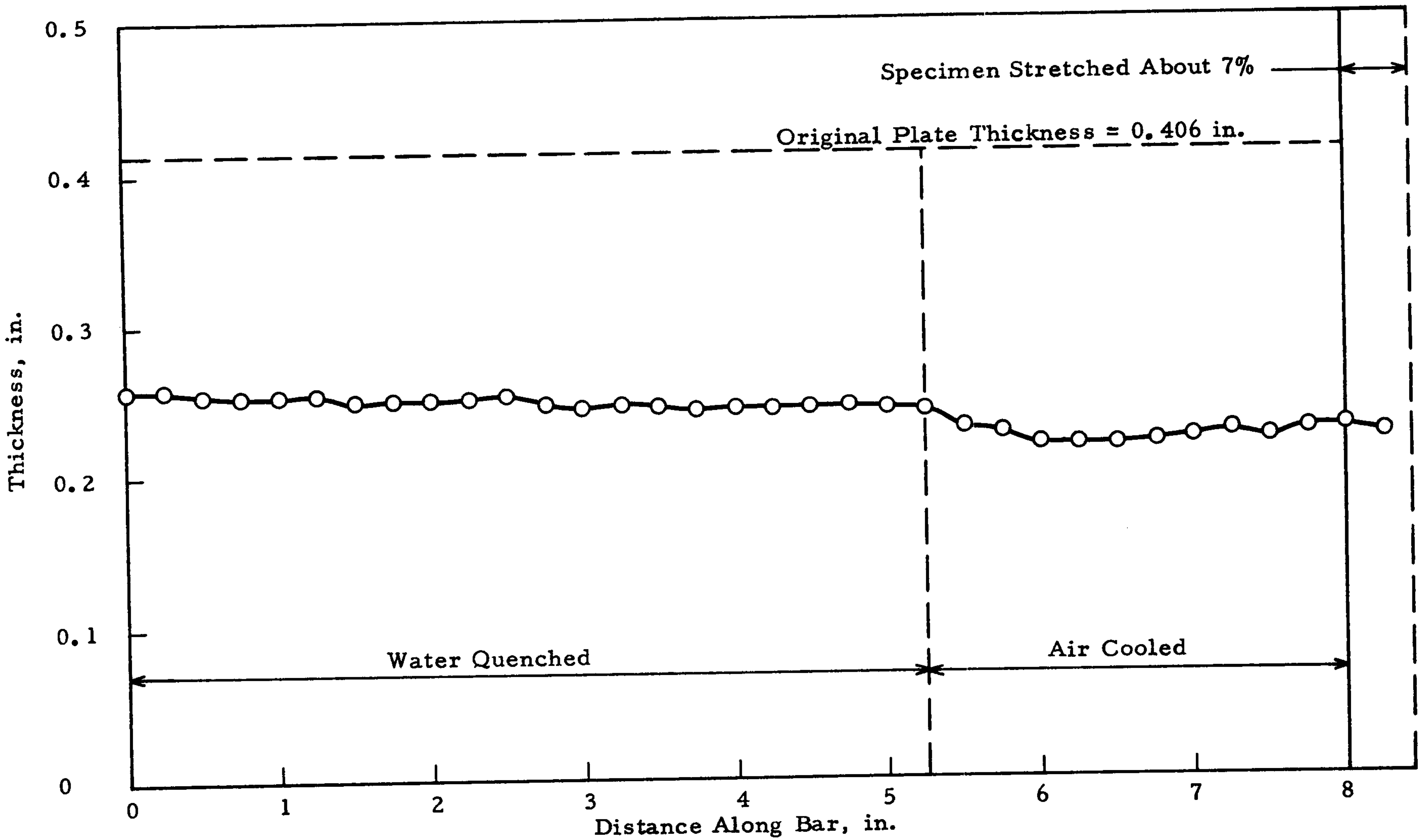


FIG. 21— MILLING PROFILE FOR SPECIMEN C2 - P-PHENYLENE DIAMINE

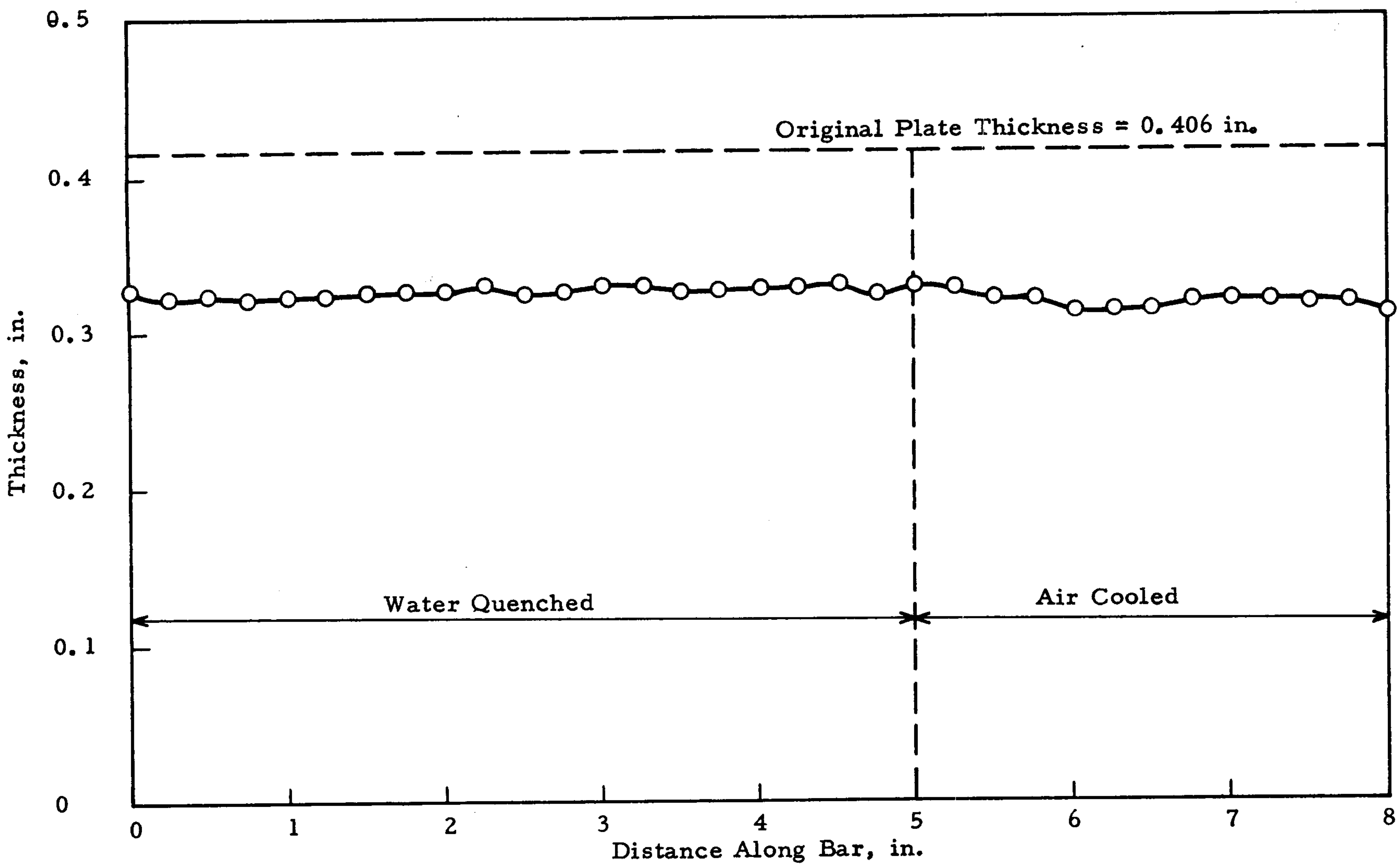


FIG. 22 - MILLING PROFILE FOR SPECIMEN 22 - TETRAETHYLENE PENTAMINE

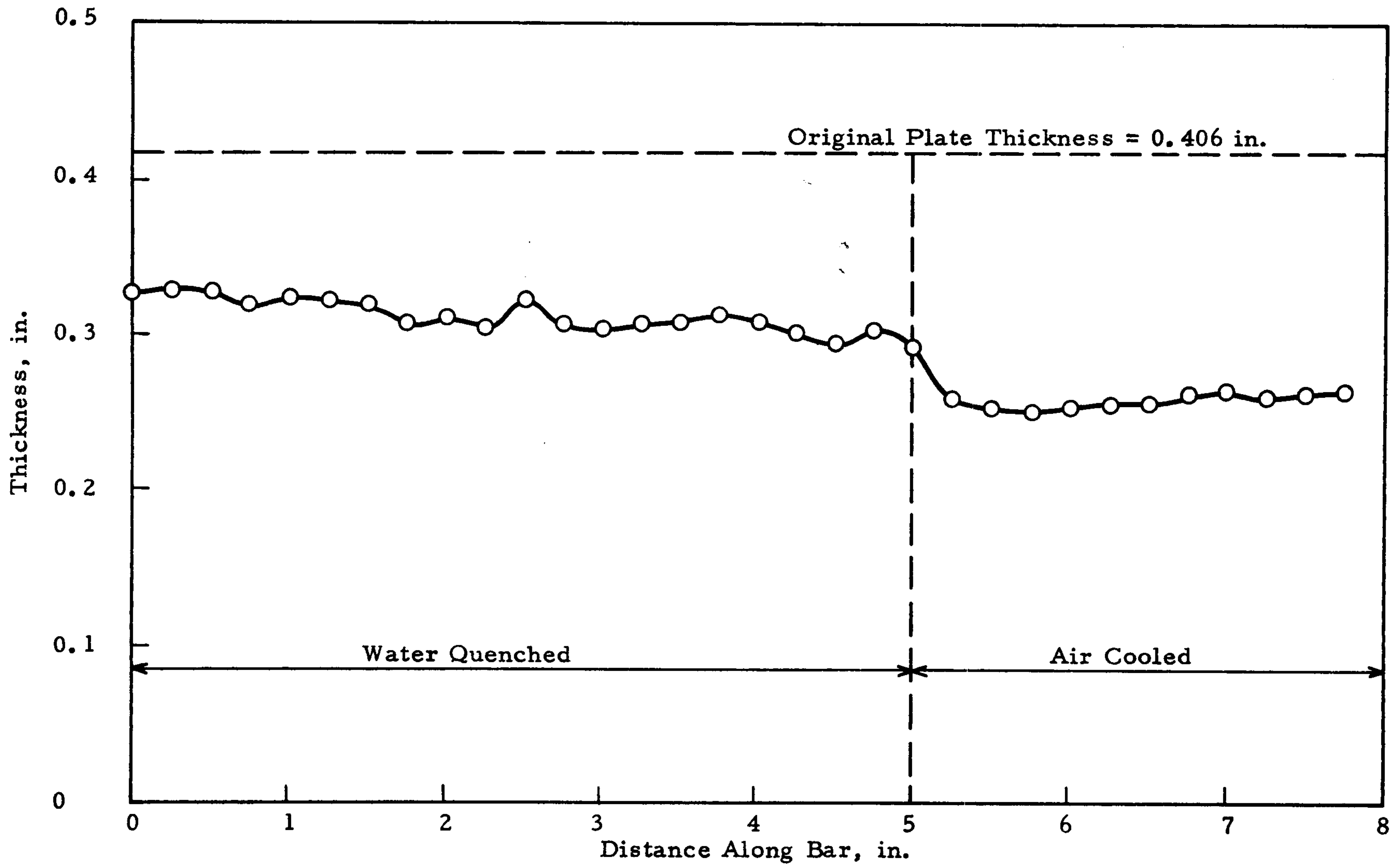


FIG. 23 - MILLING PROFILE FOR SPECIMEN C21 - 1,6 HEXANEDIAMINE

the thickness and contour of which was recognizable as that of the original specimen. The texture of this residual material was semi-pasty, and bore no resemblance to metal. It could be plowed away from the metal surface with a fingertip, and had the consistency of heavy tooth paste.

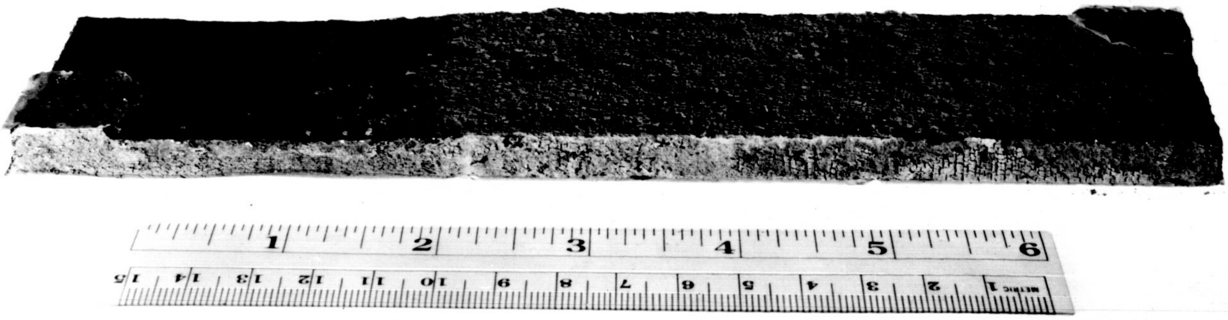
The important point, however, is that the adhesion of the smut in the water-quenched zone was not consistent. Large patches would dislodge during milling, while other areas would remain undisturbed. The effect of these patches of clinging smut was to reduce the rate of metal removal immediately under the heavy smut coating, as will be shown.

Figure 24 shows a specimen which was milled in NaOH and allowed to dry without de-smutting. The right side (water-quenched) shows a heavy layer of smut; the left side shows only a very light, dust-like residue.

The marked effect of smut adhesion on milling rate is shown in Figures 25 and 26. The specimen was milled in NaOH for 120 min, rinsed carefully, and de-smutted on only one side of the center line (the upper half of the specimen in Figure 25). It was photographed while still wet, then dried, sectioned, and measured.

The relationship between smut adhesion and depth of milling is very clear. In the central region, where the accumulated smut fell off during the immersion period, the depth of attack is considerably less than in the "no-adhesion" zone, but definitely greater than in the region of total adhesion.

The nature of the smut layer is interesting. As mentioned earlier, it is certainly not solid; it can be removed easily with a finger. However, the tenacity with which a relatively thick smut layer can cling to an aluminum surface in the presence of violent evolution of hydrogen is quite striking.



Neg. No. 27681 Specimen C3

FIG. 24 - SMUT DEPOSIT ON CHEMICALLY-MILLED SPECIMEN RINSED AND DRIED WITHOUT DE-SMUTTING. Left end was air-cooled.

Neg. No. 27682 Specimen A14

FIG. 25 - PARTLY DE-SMUTTED BAR, SHOWING EFFECT OF SMUT ADHESION ON MILLING RATE. Arrow indicates area in which the smut remains at original elevation of the metal surface. (See Figures 26 and 27.) Right end was air-cooled.

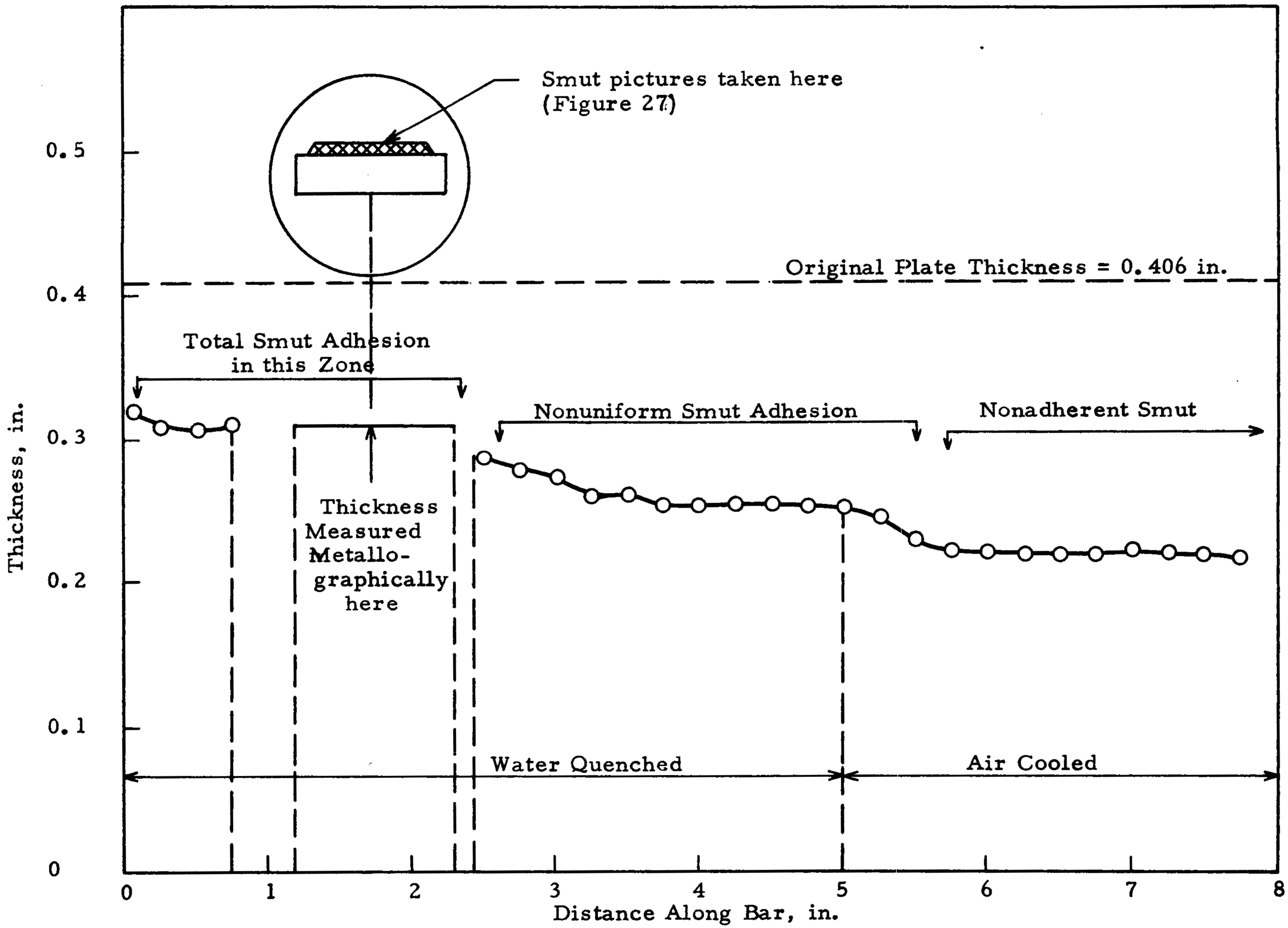


FIG. 26 - MILLING PROFILE FOR SPECIMEN A14, SHOWING EFFECT OF SMUT RETENTION ON MILLING RATE

2. Structure

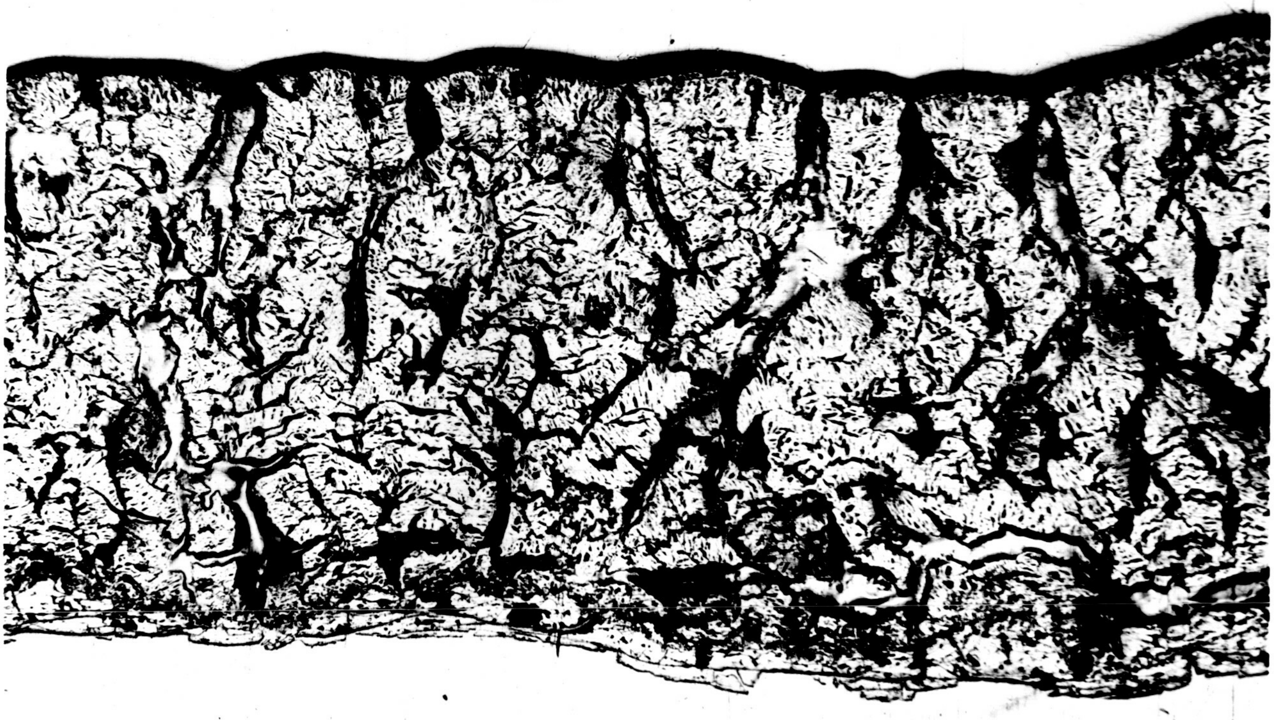
In an effort to learn if the smut has any semblance of "structure," the section shown in Figures 25 and 26 was made. The smut-covered metal was dried carefully, vacuum impregnated with cold setting clear resin, sectioned, and polished by the usual metallographic procedures. The smut is shown at two magnifications in Figure 27.

No very dramatic comments can be made about these pictures. The nature of the material itself can only be surmised; it probably contains copper and iron. The important point is that such a thick blanket of semi-permeable, but self-supporting material must certainly influence the rate of diffusion of the milling solution to and from the metal surface. In fact, we should expect to get a very similar effect if a piece of blotting paper were held against the aluminum during chemical milling--even pure aluminum.

3. De-smutting Rate; Smut Composition

When specimens were immersed in nitric acid for de-smutting, the air-cooled ends were cleaned in a few seconds. The water-quenched ends, however, required several minutes for complete dissolution of the black deposit. Pure copper, under the same conditions of exposure, was attacked extremely rapidly. It is reasonable to conclude, therefore, that the smut which is formed when Type 2219 alloy is chemically milled in plain sodium hydroxide is probably a mixture of copper, iron, and any other metallic components of the alloy which are capable of existing in strong alkali.

No complete theory will be offered for the generation of the smut, but it is reasonable to suppose that it might involve dissolution of the aluminum matrix and redeposition of the more noble elements, perhaps in the form of a "binder" for the remaining smut components (undissolved particles from the original structure).



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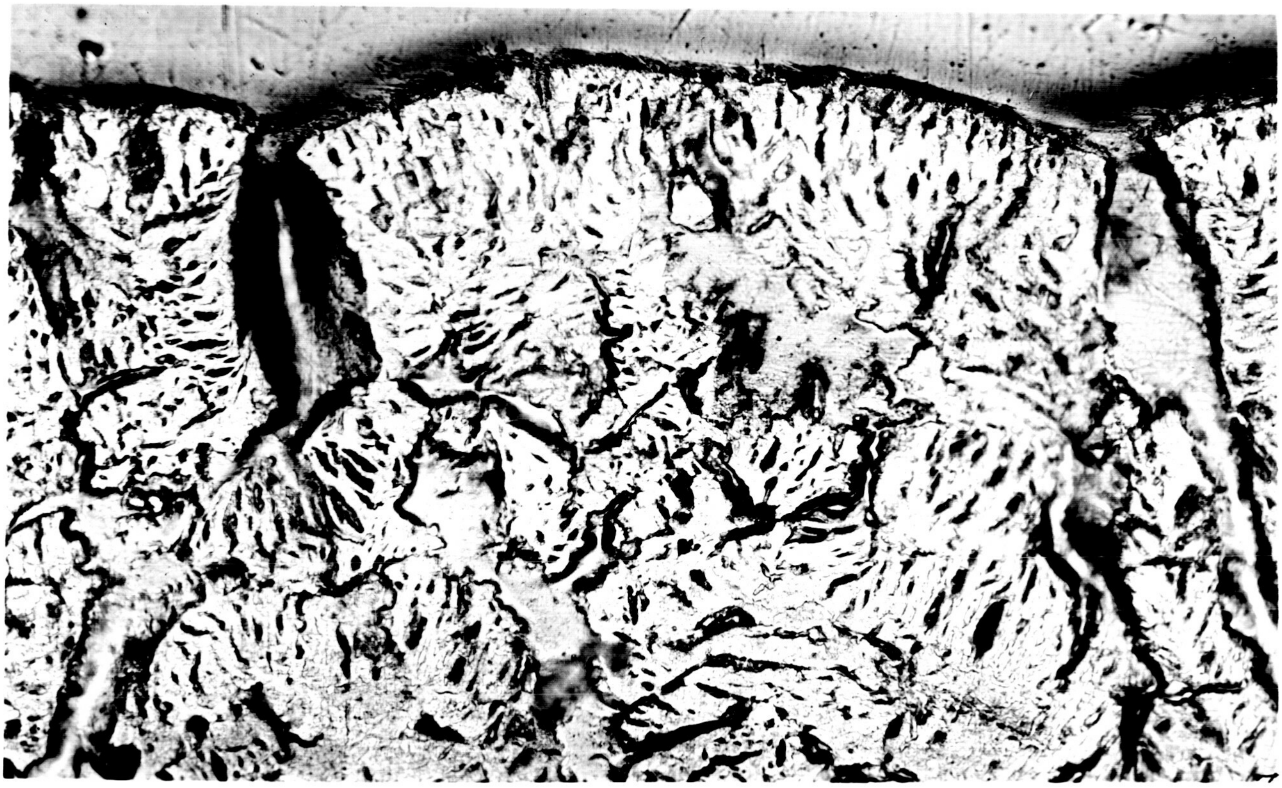

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FIG. 27 - CROSS SECTION OF SMUT DEPOSIT FROM SPECIMEN SHOWN IN FIGS. 25 AND 26.

4. Chem-Milling in Turco No. 13B Solution

In order to compare the smut adhesion characteristics of NaOH solution with commercial Chem-Mill solution, specimens of nonuniformly quenched Type 2219 alloy were processed in a Turco 13B bath. The profile obtained after exposure for 150 min is shown in Figure 28. The absence of a step is apparent. It was also noted when the specimen was removed from the bath that a uniform smut was present all over the bar.

Time did not permit further investigation of the Turco smut, but it is reasonable to assume that agents in the bath act to retain the smut components more securely--even in the air-cooled zone--than is possible in simple NaOH solutions.

V. DISCUSSION AND CONCLUSIONS

A. Metallurgical Condition of the Alloy

The development of a "synthetic" specimen for the study of nonuniform chemical milling of Type 2219-T37 aluminum alloy has made it possible to simulate the random thickness variation experienced in production. The cause of this variation is probably nonuniform quenching of the solution-treated plate. Because the alloy is so high in alloying elements--particularly copper--not all of the alloy ingredients are brought into solution. When this material is quenched, it is reasonable to believe that minor variations in cooling rate can significantly affect the distribution of material rejected from the aluminum solid solution.

It is not, of course, clear how this metallurgical variation affects the chemical milling characteristics of the plate, but the results obtained indicate that it is the smut variation that is responsible for the differences in rate of attack, rather than a basic difference in the anodic propensity of the alloy itself.

B. Cause of Variations in Milling Rate

Measurements of electrode potential during milling show, in fact, that an extremely slight difference in activity exists between

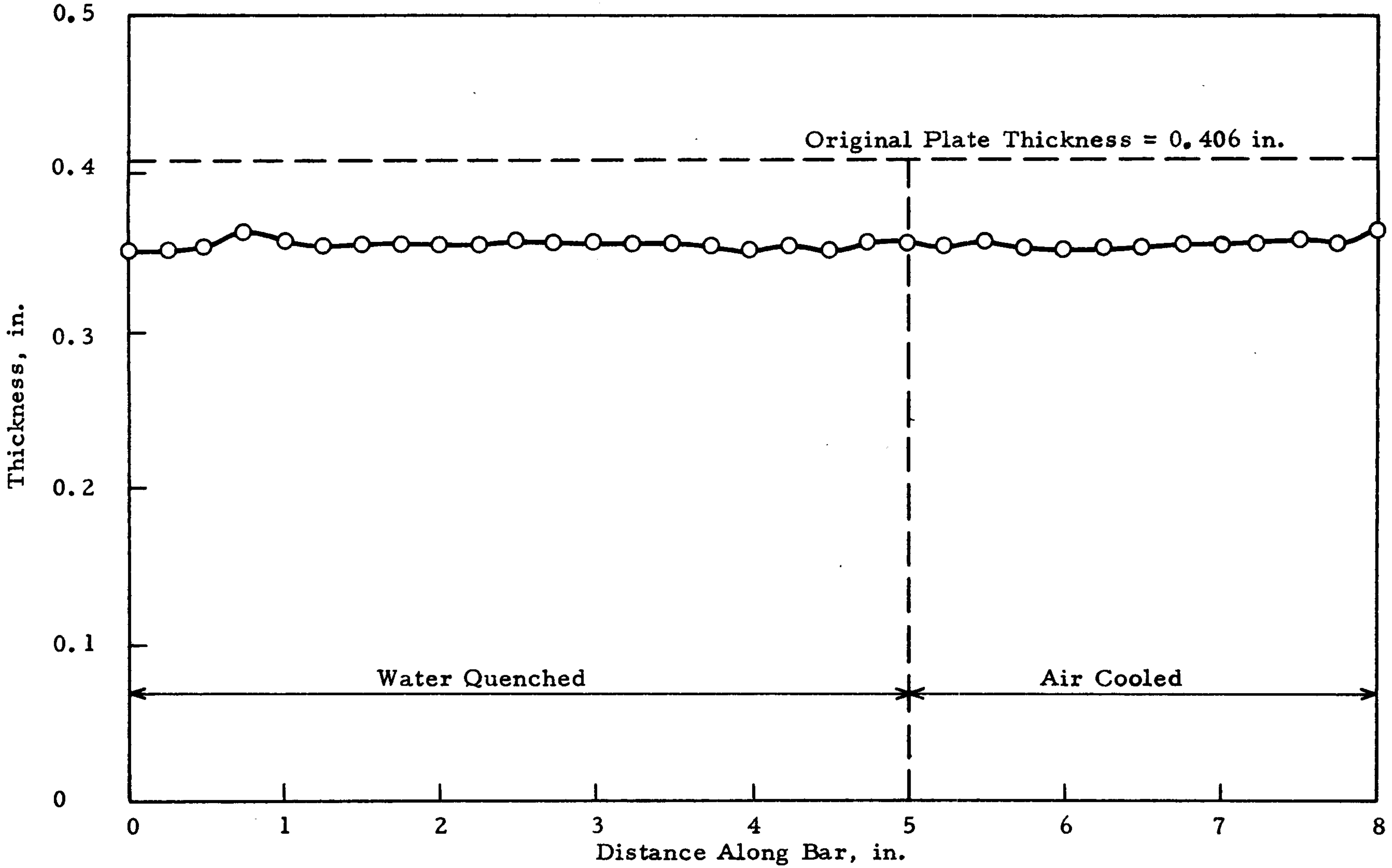

FIG. 28 - MILLING PROFILE FOR SPECIMEN C17 - TURCO 13B

water-quenched and more slowly cooled regions. The difference is probably not sufficient to account for the variations in milling rate. The variation in etch rate observed within the water-quenched zone of laboratory specimens was positively correlated with the variation in smut retention.

C. Effect of Additives

As discussed earlier, the philosophy used in planning this program was to add chemicals to the milling solution which would cause ready dissolution of copper, thereby erasing any inherent differences in basic activity of the metal in various regions.

None of the additives produced satisfactorily uniform dissolution of the (grossly inhomogeneous) synthetic specimens, but the tetraethylene pentamine showed improvement over plain NaOH (Figure 22). This compound should be studied further.

VI. RECOMMENDATIONS FOR FURTHER WORK

While the nonuniform quenching technique described and used in this work has made it possible to screen experimental solutions rapidly, a modified nonuniform quench should be devised which will more closely simulate the variations possible in the production of the plate. In other words, the sensitivity of the alloy to quenching should be studied so that it can be determined if very minor quenching irregularities can in fact cause nonuniform milling.

For this purpose a bar specimen would be used (as in the present work), but quenching would be accomplished by a spray method, in which a zone of less rapid quenching could be induced by (perhaps) blocking a small region of the spray pattern. It is important to determine if the (rather large) effects observed in the present specimen will persist when only small thermal inequities exist from spot to spot on the specimen surface.

The nature of the smut formed during chemical milling should be investigated further, particularly with respect to its copper, iron, and aluminum contents. It will also be valuable to learn how it is held together with sufficient strength to resist the scrubbing action of hydrogen. Even more important, it should be learned how the cohesive properties of the smut can be so different on water-quenched compared to air-cooled zones. The gross composition of the two regions is, after all, the same; only the microstructure can vary.

Finally, a different approach to the attainment of uniform milling should be attempted. Whereas, the present attack on the problem was aimed at increasing the ease of dissolution of the metallic constituents, thereby preventing smut formation, a more promising approach might be to add metallic constituents to the bath, selected to cause a uniform smut to appear on all parts of the metal surface. If a sufficiently uniform "porous pad" could be generated everywhere on the metal, uniform--although perhaps, slower--milling might result.

VII. LOGBOOKS AND CONTRIBUTING PERSONNEL

Data used in the preparation of this report are recorded in IITRI Logbook Nos. C15244 and C15517.

Personnel contributing to the program included: Howard T. Francis, Manager, Electrochemistry; William H. Graft, Research Metallurgist; John C. Kaminski, Technician; and Robert E. Wheeler, Associate Mathematician.

Respectfully submitted,
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