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INVESTIGATION OF THE MECHANISM OF
STRESS CORROSION OF ALUMINUM ALLOYS

Bureau of Naval Weapons Contract N0w64-0170c

First Quarter Report

(Period of December 6, 1963 to February 29, 1964)

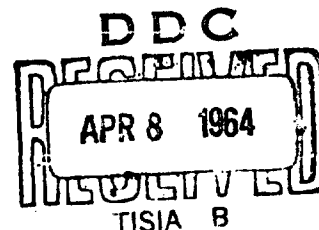
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SYNOPSIS

(1) Methods have been developed to utilize the standard 1/8-inch diameter tensile bar and stressing fixture for conductivity studies to establish the cathodic protection criterion for both unstressed and stressed specimens.

(2) An anodic polarization technique that shows promise for evaluating the interaction between metallurgical structure and electrolyte has been developed. There are two important factors in the technique: (a) an anodic pretreatment to develop active, localized attack characteristic of the metallurgical structure and (b) a rapid scanning rate to evaluate this localized attack before it is stifled by film repair.

INTRODUCTION:

This report summarizes the work during the period, December 6, 1963 to February 29, 1964. In this period, 174 man hours were spent on the contract.

MATERIALS:

The 0.250-inch thick 2024-F and 7075-F alloy plate described in the proposal have been obtained from regular plant production; and samples of this plate have been heat-treated and aged in the laboratory to produce several metallurgical conditions reflecting a range of susceptibility to stress corrosion.

CATHODIC PROTECTION STUDIES:

As outlined in the proposal, cathodic protection is to be used to establish the potential of the most anodic phase in each alloy. Electrical conductivity has been selected for following the course of corrosion during cathodic protection. Measurement of this conductivity requires some method for attaching electrical leads to a specimen; and for a stressed specimen, some method for insulating the specimen from the assembly used for stressing.

Percussion welding has been found to be a simple and convenient method for attaching electrical leads to the 1/8-inch diameter tensile specimens selected for the cathodic protection studies. The bond is strong enough mechanically and there is no significant damage to the reduced section of a specimen, as determined both by tensile tests and by metallographic examination.

An anodic hard coating applied to the standard fixture for stressing a sub-size tensile specimen has been found adequate for electrical insulation. Measurements in several electrolytes have shown that the assembly is satisfactory for following the course of corrosion during cathodic protection. The conductance of the electrolyte can be ignored; and the electrical conductivity can be measured with an isolating potential comparator while a specimen is being polarized cathodically with a potentiostat.

ANODIC POLARIZATION CURVES:

Work just before the contract was awarded indicated that anodic polarization curves of preconditioned specimens are useful for relating metal structure and electrolyte; and this work has been explored more fully. It has been explored more fully because a principal objective of the contract is to establish electrolytes that provide substantially different stress corrosion performance for the same

metallurgical structure. Originally, these electrolytes were to be established by cathodic protection studies; and, these studies will still be used for this purpose. At the same time, another procedure, particularly one that is much faster, should be of considerable assistance.

The technique is illustrated in Figures 1 and 2, which show anodic polarization curves for preconditioned specimens of 2024 and 7075 alloy sheet in tempers that provide a wide range of susceptibility to stress corrosion. Each specimen was first polarized anodically at a current or potential high enough to produce substantial corrosion. The objective of this pretreatment was to produce highly developed, active sites of attack. A polarization curve was then established by scanning rapidly with a potentiostat in a more negative direction from the preconditioning potential to the potential at zero current; or alternatively, it was established by re-scanning rapidly in the opposite direction from the potential at zero current to the preconditioning potential.

As is clear from Figures 1 and 2, each polarization curve consists of two, nearly linear branches. For the 7075 alloy specimens in Figure 1, these branches are well developed with a reasonably sharp intersection between them.

The curves for the 2024 alloy specimens in Figure 2 are somewhat less well developed and the intersection between them is not quite so clearly defined. In this case, the intersection has been indicated by extrapolation of the linear portions of the two branches.

Only the lower branch of each polarization curve reflects the highly developed sites of attack. Establishing this branch requires a rate of scanning rapid enough to prevent repair of the oxide film at the sites of attack. The effect of the sites of attack on the upper branch of each polarization curve is obscured by a second highly unpolarized reaction.

The most important feature of these polarization curves is their relationship to the type of attack (which is indicated in the captions for Figures 1 and 2), and to stress corrosion behavior. This point is illustrated by a comparison of the currents at which the two branches of each polarization curve intersect. For both 2024 and 7075, a higher current is indicative of a greater tendency to intergranular attack; and the items showing the higher currents are in the tempers which would be expected to have the least resistance to stress corrosion. Not so obvious perhaps, is the fact that the area between the

lower branch of the polarization curve and the potential axis rates the tempers in the same order as the current indicated by the intersection of the two branches. This area is affected by both the current density and the potential range and both of these factors tend to change in the same direction. Therefore, the area may be preferable to the current in some instances for comparing two tempers.

Another important feature of the curves is that the lower branches for each alloy intersect the zero current density axis at about the same potential. This suggests that the anodic regions in the various tempers of each alloy are substantially the same. The small differences observed may be related to differences in the nature of the attack. For example, specimens with intergranular attack tend to have the most anodic potential and these specimens are precisely the ones that would be expected to retain the acidity of the anolyte for the longest period.

A final feature of these curves is that the upper branches are displaced toward more negative potentials by artificial aging. The extrapolated intercepts of the upper branches with the potential axis fall in the same order as conventional solution potentials. For 2024, this certainly reflects the amount of copper remaining in solid

solution. Although precipitation is more complex for 7075 alloy, the more negative intercepts shown by the -T6E106 and -T73 tempers also suggests the influence of copper.

Polarization curves of the type described here are influenced by the pretreatment used, and by the scanning rate and its direction. A comparison of Figures 2 and 3 illustrates the effect of scanning direction. For the curves in Figure 2, the specimens were scanned in the negative direction following pretreatment. These specimens were then scanned in the positive direction to obtain the curves in Figure 3. As can be seen, the only significant effect of scanning direction was to shift the curves along the current density axis. It did not affect their relative order, but it did affect their separation and the sharpness of the intersection of the two branches.

A comparison of Figures 3 and 4 shows the effect of preconditioning. The curves in Figure 4 were obtained by preconditioning at a constant potential while those in Figure 3 were obtained by preconditioning at a constant current. Again, the effect was to shift the curves along the current density axis but not to change their relative order.

Obviously then, the curves do not reflect absolute measurements and conditions must be selected judiciously to exaggerate the difference of concern. For example, the intersections of the curves in Figure 3 are better defined than those in Figure 2. But, the separation of the curves is better in Figure 2, especially when this separation is evaluated by area between the lower branch and the potential axis.

The usefulness of the curves in selecting electrolytes is illustrated further by Figures 5 and 6. The curves in Figure 5 illustrate the effect of increasing the pH of the 3-1/2% sodium chloride solution used for the curves in Figures 2 to 4. As can be seen, the effect of increasing the pH was to decrease, for all of the 2024 alloy specimens, the current defined by the intersection of the two branches of the polarization curves. This decrease is in agreement with general experience that alkalinity decreases susceptibility to stress corrosion of aluminum alloys.

The curves in Figure 6 for sodium sulfate provide even more striking evidence of the effect of electrolyte. In this case, the current density was several orders of magnitude lower than that for sodium chloride, and there were no breaks in the polarization curves even though the

specimens were preconditioned at highly positive voltages. In sodium sulfate, film formation apparently proceeded so rapidly that active sites of attack were not produced.

FUTURE WORK:

Less time was spent on the contract in the first quarter than would be expected on a prorated basis; but this less-than-average activity can be compensated for easily in the next quarter.

Immediate attention is being given to the cathodic protection studies for the variety of metallurgical conditions of both alloys that provide a range of susceptibility to stress corrosion. The anodic polarization technique developed in the first quarter will be used to assist in selecting electrolytes that provide a difference in stress corrosion performance for the same metallurgical structure. It is expected that most of the cathodic protection studies can be completed for both stressed and unstressed specimens.

In the next quarter, also, it is expected that many of the metallurgical features of the various samples can be elucidated and correlated with stress corrosion behavior. Examination with the light and electron microscope will be started concurrently with the cathodic protection studies.

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Figure 1

Anodic polarization curves for 7075

Electrolyte	3-1/2% NaCl
Pretreatment	20 minutes at 10 milliamperes per square centimeter.
Scanning Rate	200 millivolts per minute, positive direction.

<u>Temper</u>	<u>Type of Attack (After Polarization)</u>
-T6	pitting + slight intergranular
-T6E106	pitting + slight intergranular
-T73	pitting

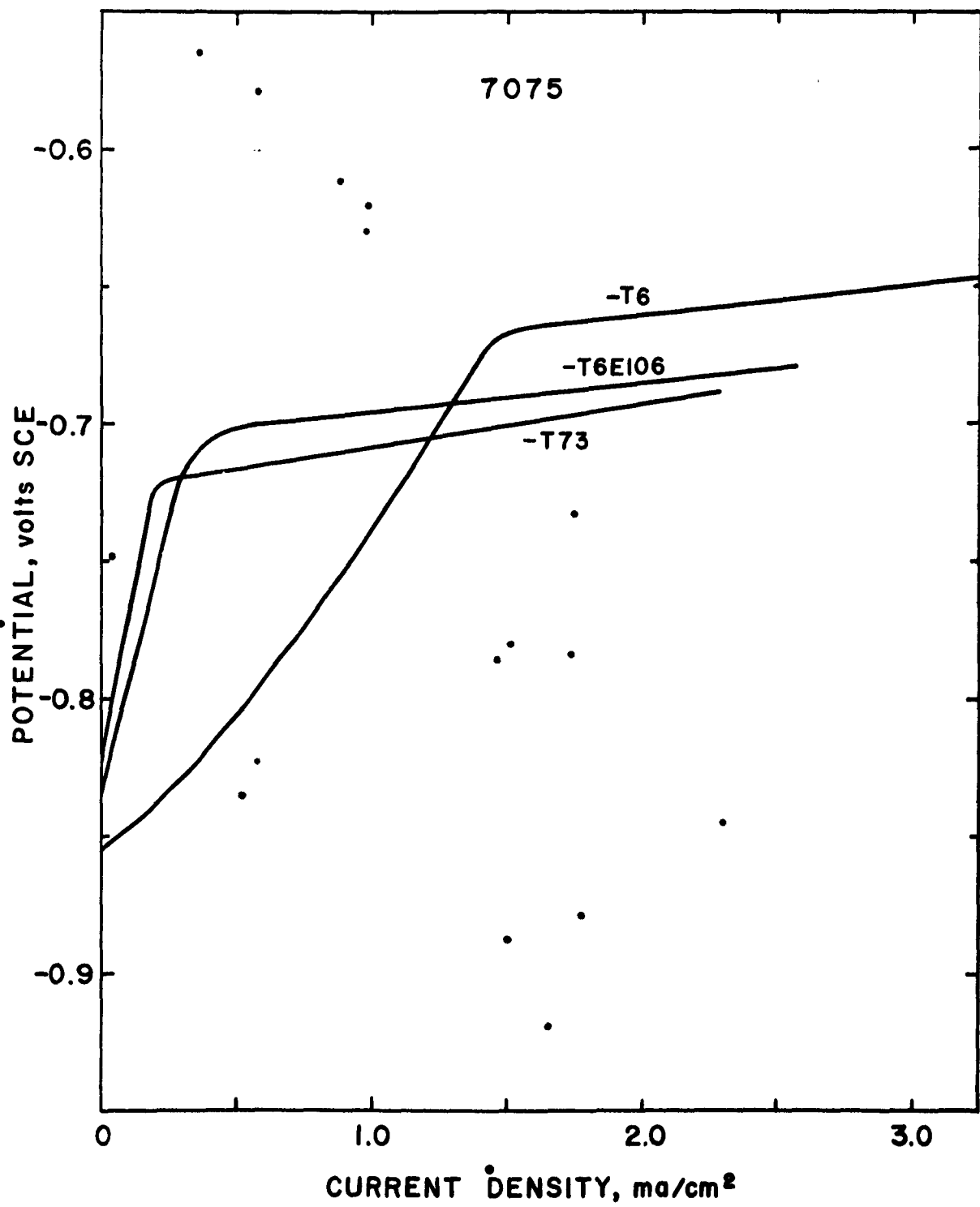


Figure 1

Figure 2

Anodic polarization curves for 2024

Electrolyte 3-1/2% NaCl

Pretreatment 20 minutes at 10 milliamperes
per square centimeter.

Scanning Rate 200 millivolts per minute,
negative direction.

<u>Temper</u>	<u>Type of Attack (After Polarization</u>
-T4 Cold Water Quench	pitting + slight intergranular
-T4 Boiling Water Quench	intergranular
-T36 + 4 hrs. @ 375 F	intergranular + pitting
-T86	pitting + intergranular

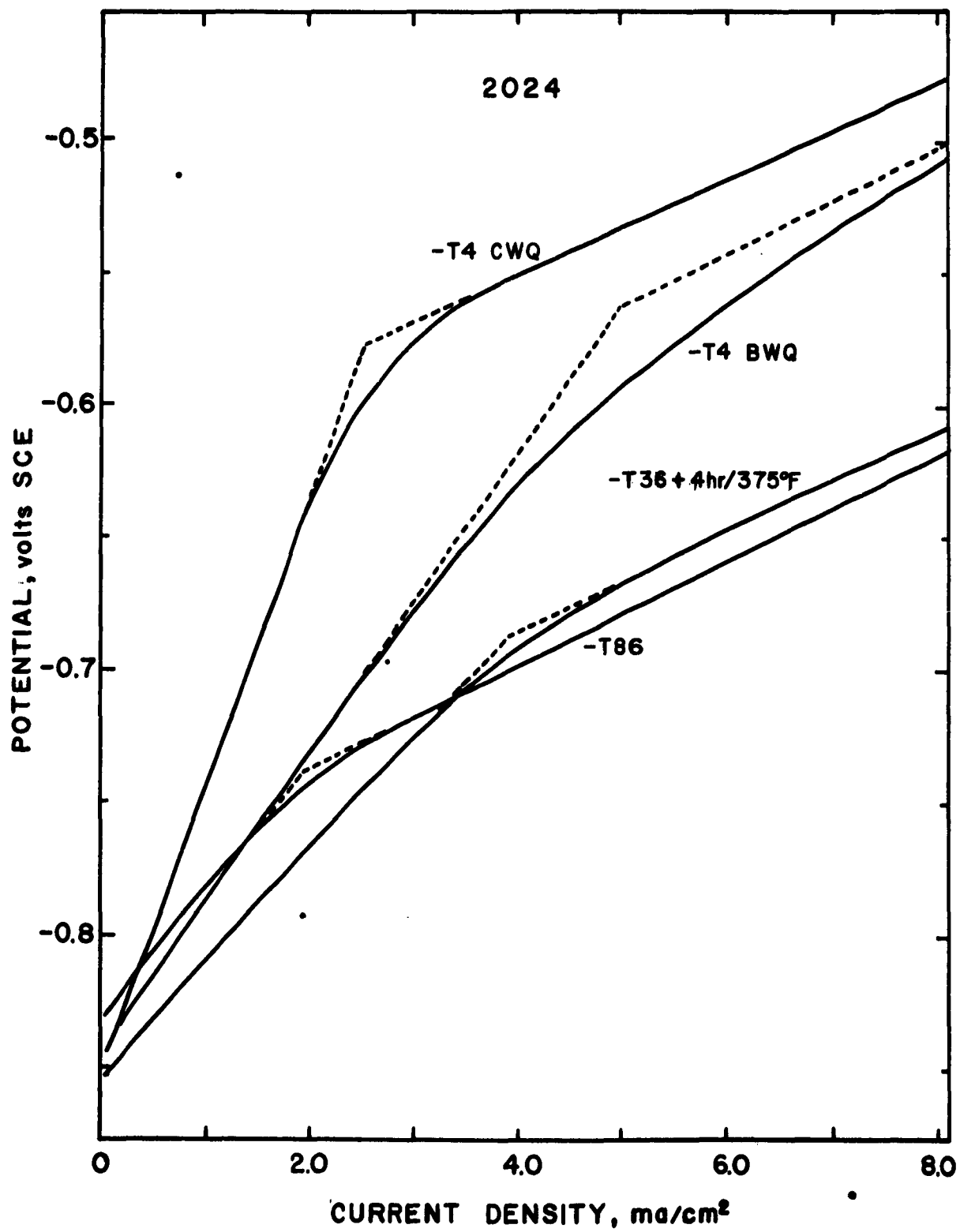


Figure 2

Figure 3

Anodic polarization curves for 2024

Electrolyte	3-1/2% NaCl
Pretreatment	20 minutes at 10 milliamperes per square centimeter.
Scanning Rate	200 millivolts per minute, positive direction.

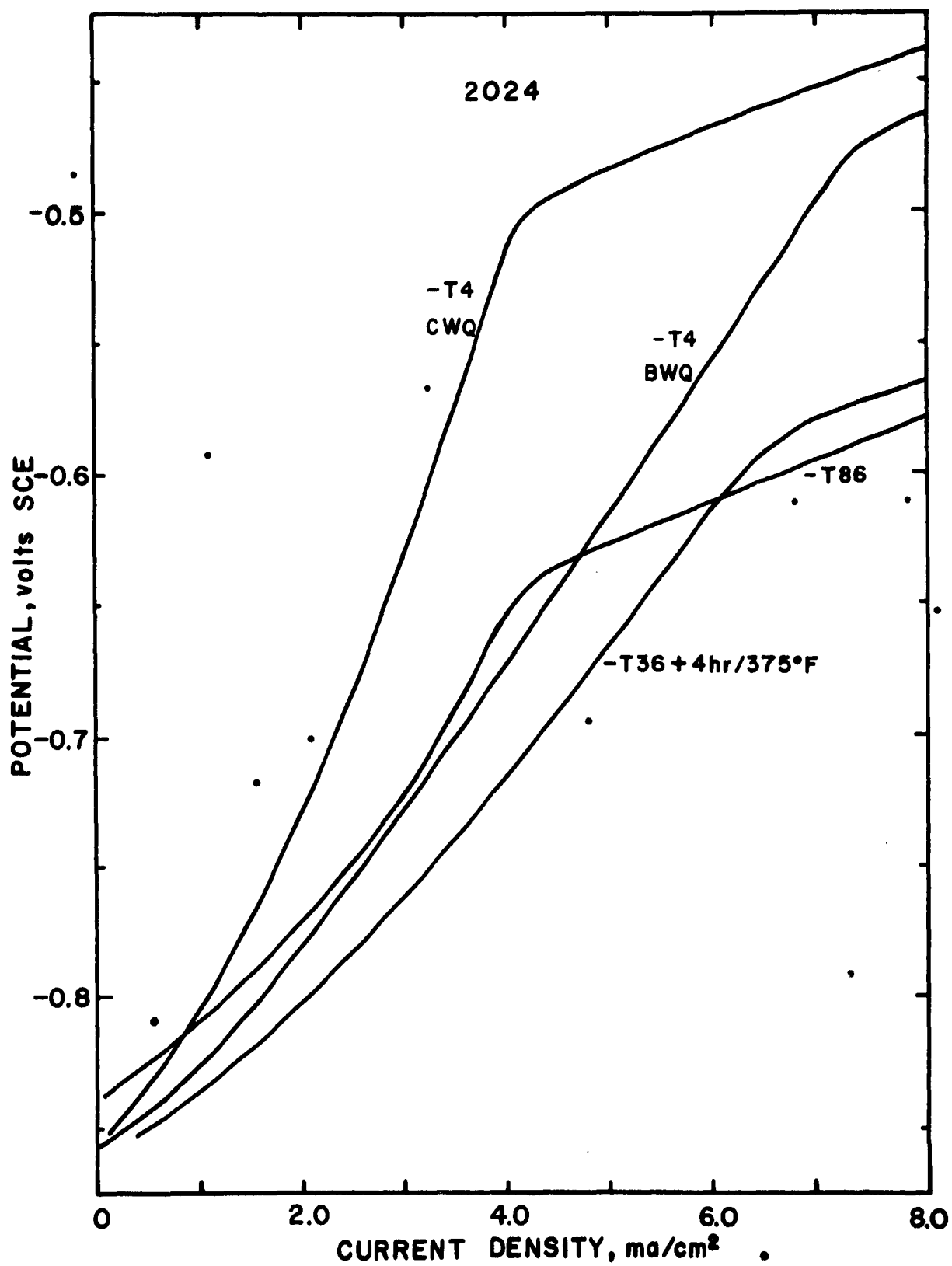


Figure 3

Figure 4

Anodic polarization curves for 2024

Electrolyte	3-1/2% NaCl
Pretreatment	15 minutes at -0.55 volts referred to Saturated Calomel Electrode.
Scanning Rate	200 millivolts per minute, positive direction.

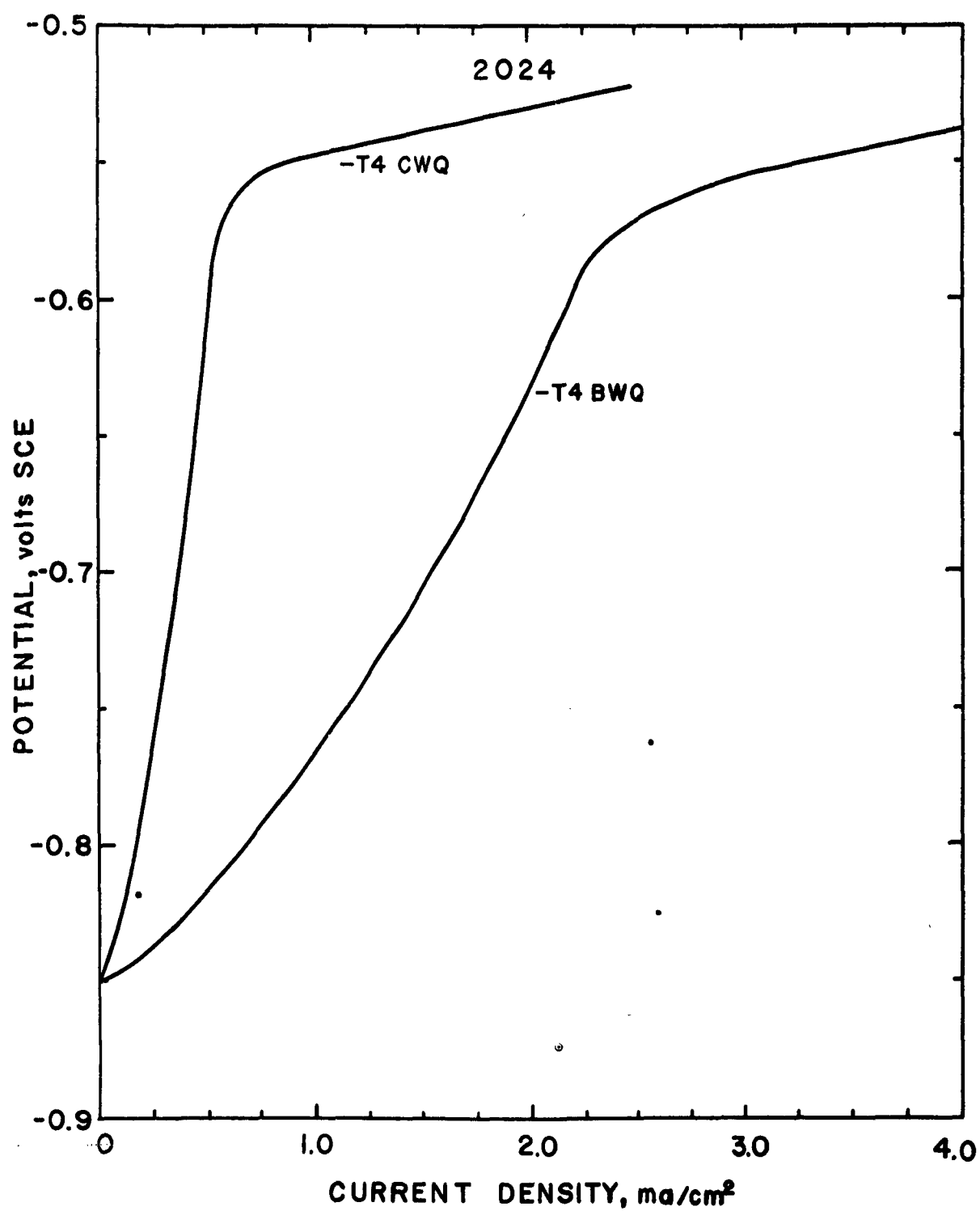


Figure 4

Figure 5

Anodic polarization curves for 2024

Electrolyte	3-1/2% NaCl, buffered at pH 9.3 with NaHCO_3 - Na_2CO_3
Pretreatment	20 minutes at 10 milliamperes per square centimeter.
Scanning Rate	200 millivolts per minute, negative direction.

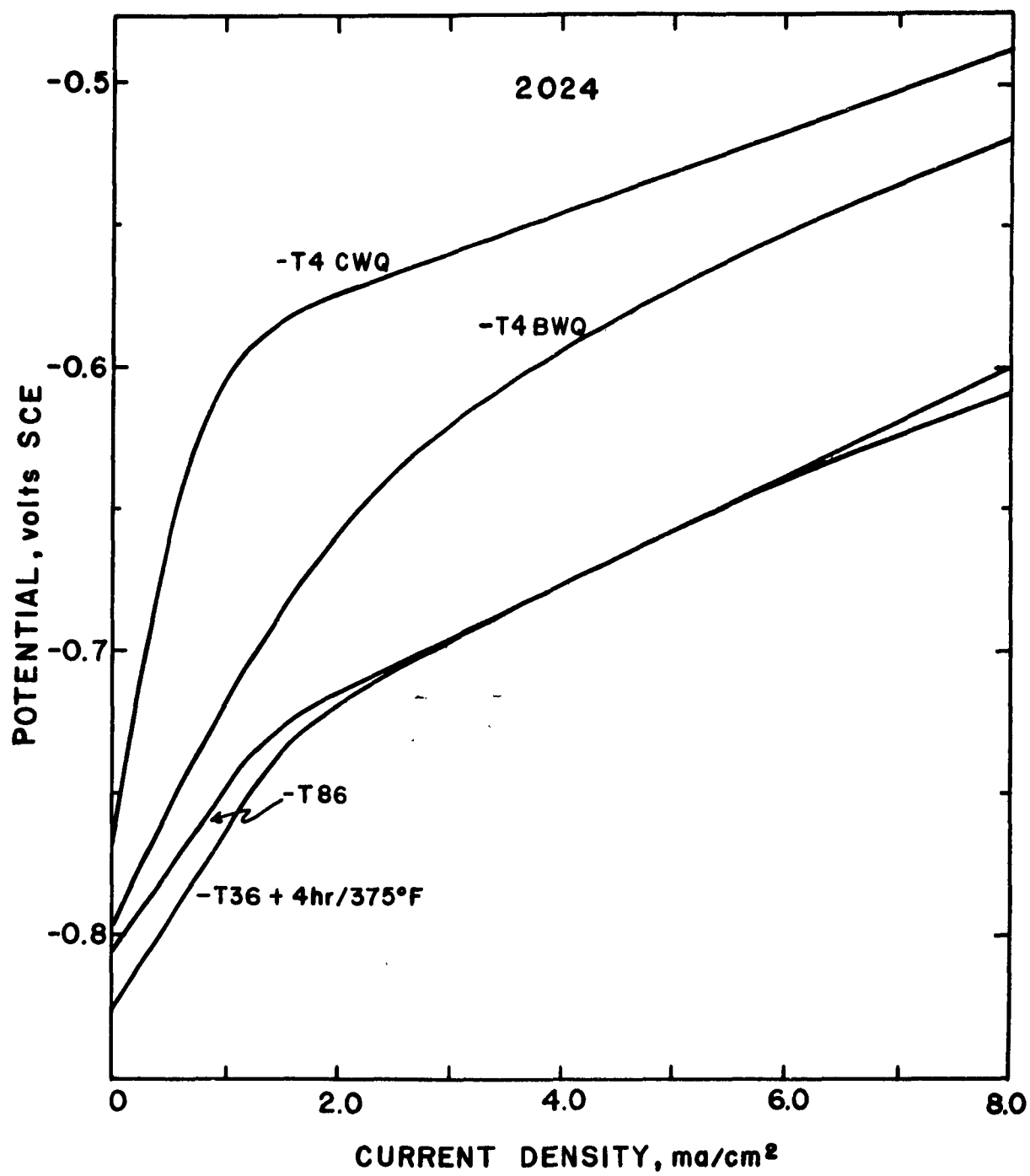


Figure 5

Figure 6

Anodic polarization curves for 2024

Electrolyte	0.6N Na ₂ SO ₄
Pretreatment	5 minutes at +0.5 volts referred to the Saturated Calomel Electrode.
Scanning Rate	200 millivolts per minute, negative direction.

Note that the unit of current density is
microamperes per square centimeter.

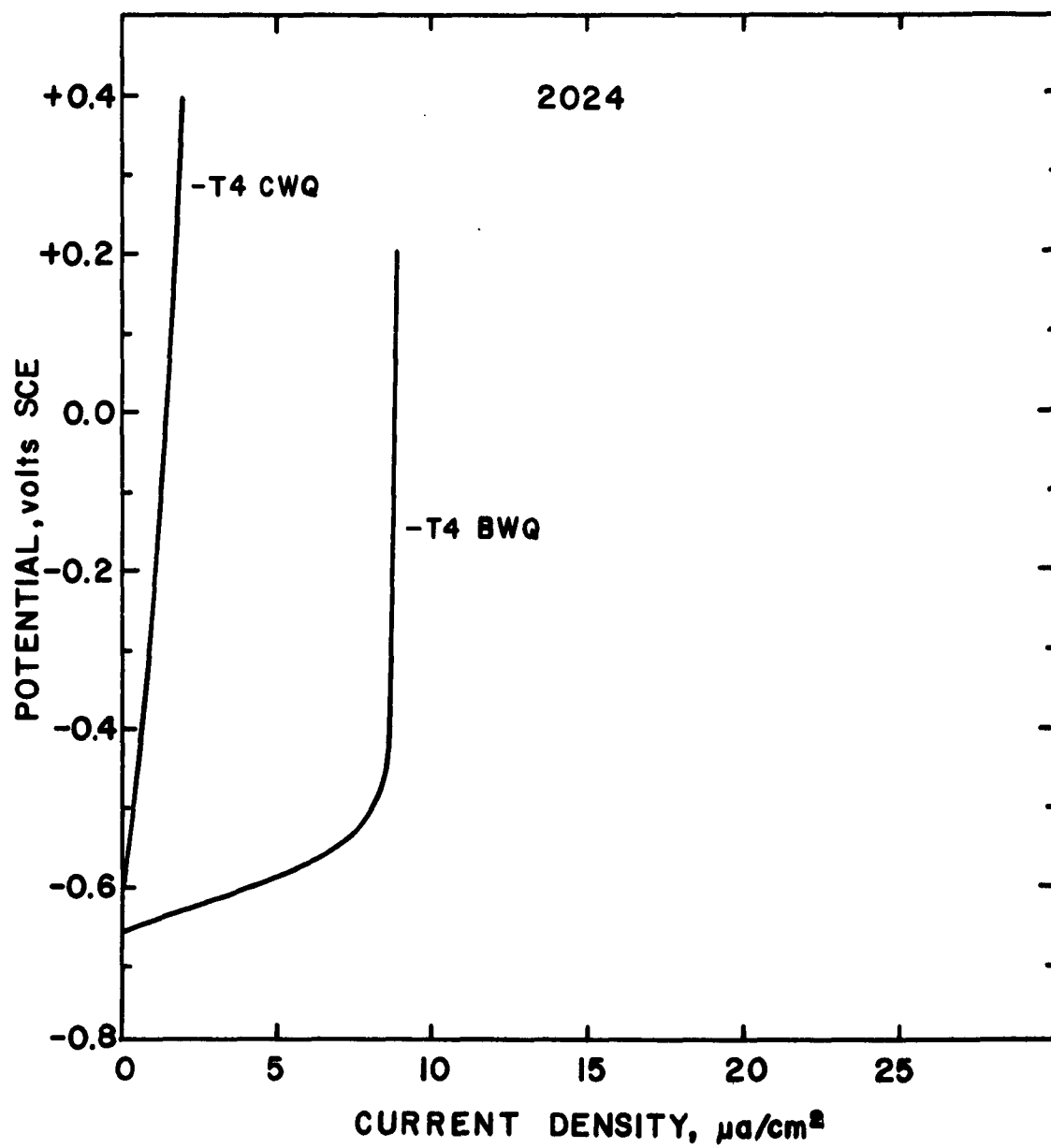


Figure 6

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