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# Marine Corrosion Studies

# Characterization of the Corrosion Behavior and Response to Cathodic Protection of Nineteen Aluminum Alloys in Sea Water

## (Seventh Interim Report of Progress)

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## ABSTRACT

The corrosion characteristics of nineteen structural aluminum alloys were studied in quiescent sea water. Some alloys were exposed with and without cladding, and others at more than one strength level for a total of twenty-six material conditions. The response to cathodic protection of all the alloys studied was also determined.

The electrochemical potentials of the alloys were monitored during the experiment and a relationship was developed between the electrode potential and the corrosion characteristics of the alloys. These mean potential values were found to differ significantly in many instances from the electrochemical potential values determined by other investigators from laboratory measurements in sodium chloride-hydrogen peroxide solution.

Cathodic protection from galvanic anodes was effective in reducing the corrosion damage to acceptable limits except edge attack was not eliminated on one of the high strength 7XXX series aluminum alloys.


## PROBLEM STATUS

This report completes one phase of the task; work is continuing on other phases.

## AUTHORIZATION

NRL Problem No. 63M04-02
Task No. SF 51-542-602-12431

## INTRODUCTION

Aluminum alloys are finding increased use in marine and ocean engineering applications because of their favorable strength-to-weight ratio. Although a number of investigators (1-7) have reported on the corrosion behavior of aluminum, only limited information is available on the behavior in quiescent sea water of the higher strength alloys hitherto used principally for aircraft applications, and almost no quantitative information is available as to the effectiveness of cathodic protection.

It was also desired to establish reliable electrochemical potential data for aluminum alloys in sea water. Most of the previously reported electrochemical potentials (8) were measured in short-term laboratory experiments in sodium chloride solutions containing hydrogen peroxide.

Electrochemical potential data are required for several reasons: The values so measured (1) establish the potential for a given alloy and any galvanic anode used for cathodic protection must have a more negative potential, (2) offer an initial guide to the selection of compatible alloys, i.e., alloys none of which will suffer accelerated corrosion when coupled in a multi-alloy structure, and (3) provide a basis for developing a means for predicting long-term corrosion behavior from short-term electrochemical measurements.

For these reasons a broad-spectrum study of aluminum alloys was initiated. Nineteen structural alloys were included in this study. Some alloys were available with Alcladding or in several hardness levels. A total of twenty-six material conditions were studied (Table 1). In addition, one proprietary aluminum alloy anode with a known stable electrochemical potential was included as a control.

## PROCEDURES

The experiment was conducted at the Naval Research Laboratory's Marine Corrosion Research Laboratory,

Key West, Florida. The exposure racks were suspended under a pier in quiescent, but not stagnant, sea water. The water characteristics during the period of interest were as follows:

| | |
|---|---|
| Temperature: | 16.5 to 32.5°C (61.7-90.5°F) |
| Resistivity: | 16 to 21 ohm-centimeters |
| pH: | 8.2 |
| Oxygen: | Not measured, but assumed to be saturated |

The specimens used in the study measured 6 x 12 in. except for the 5052-H32 panels which were 5-in. wide, and the 7079-T6 panels which were 4-in. wide. Specimens were cut from commercially supplied stock which varied in thickness from 0.050 to 1 in. To expedite the experiment materials were exposed in the as-rolled thickness. Specimens were attached to painted aluminum racks with nylon bolts, nuts, washers, and insulating strips. The artificial crevices formed at the attachment points were utilized to assess the susceptibility of the aluminum alloys to crevice corrosion. Duplicate specimens were exposed for each material condition. One specimen was exposed unprotected and the second specimen was provided with a 1/2 x 1 1/4 x 6-in. aluminum alloy anode. An anode of this size was sufficient to polarize the protected specimen to approximately minus 1.1 volts to a Ag/AgCl reference electrode. The crevices formed at the interfaces of the anodes and the aluminum specimens were sealed to prevent a build-up of corrosion products benind the anodes which could have caused mechanical detachment of the anodes.

An insulated electrical test lead was attached to each specimen to allow the measurement of the electrochemical potential relative to a remote Ag/AgCl reference electrode. The potential of each specimen was measured weekly for the first 63 days. The potentials of selected specimens were measured for longer times, in some instances up to 360 days of the 368-day experiment.

At the conclusion of the exposure period, the gross marine fouling was removed from the specimens with a high-pressure water jet, and the specimens were chemically cleaned in a 2 percent chromic acid-5 percent phosphoric

acid solution maintained at 80-85°C. The corrosion on all specimens was characterized by visual inspection and by measurement of the depth of attack with a dial gage micrometer.

## CORROSION CHARACTERISTICS

### Criteria for Corrosion Resistance

The choice of the most meaningful parameter to characterize the corrosion behavior of an alloy is in large part dependent upon the end use contemplated for the material. Although weight loss or "average corrosion rates" in inches penetration per year might be quite useful in estimating the life of a massive pier structure constructed of mild steel, the same type of data would be meaningless if used to estimate the life of an aluminum instrument package in which the most likely mode of failure would be perforation due to preferential attack or pitting.

In many instances it is, therefore, meaningless to report data based on weight loss for materials which do not corrode uniformly, because such data are of little or no value to the designer and might readily mislead an unwary novice into a poor material choice.

Three parameters were used to characterize the corrosion attack on the aluminum alloys of the present study. They were:

1. The deepest attack in the crevice formed by the plastic mounting attachments.

2. The deepest attack on the surface of the specimen not associated with any known crevice.

3. The mean value of the five deepest points of attack regardless of location.

In addition, some of the alloys studied developed edge cracking in the form of exfoliation or delamination. The

depth of this type of corrosion could not be accurately determined, but the presence of such attack has been noted.

Depth of Attack on Aluminum Alloys in 368 Days in Quiescent Sea Water

Quantitative depth of attack data for each material are shown on Fig. 1-5. These data are arranged using The Aluminum Association's designation for the alloys. The figures show not only the depth of attack on the unprotected alloy, but also the degree of reduction of attack obtainable through the use of cathodic protection.

Alloys X7002-T6, 7178-T6, and Alcad 7178-T6 developed edge cracking during the exposure period. These data are noted on Figs. 4 and 5, but no quantitative estimate of the degree of attack was feasible. Edge cracking of the X7002-T6 alloy was eliminated by either Alcladding or cathodic protection (Fig. 6), but neither of these techniques was adequate to completely eliminate this type of attack on the 7178-T6 alloy (Fig. 7).

The corrosion behavior of the aluminum alloys and their response to cathodic protection are summarized in Table 1 where the alloys have been separated into groups according to the mean depth of attack. The group of alloys showing the greatest inherent corrosion resistance includes many of the 5XXX series alloys. However, the X7005-T63 and 7106-T63 alloys were more corrosion resistant than had been expected and the data from this study place them in the most corrosion resistant group.

The effect of the hardness condition of aluminum alloys on their corrosion characteristics is demonstrated by the 6061 alloy. In the T651 condition, this alloy was among the most corrosion resistant studied with a mean depth of attack of less than 1 mil and with no evidence of crevice corrosion. In contrast, in the more common T-6 condition the mean depth of the five deepest points of attack was 8 mils with a maximum depth of attack of over 10 mils. These same effects were not evident in the strain hardened alloys, i.e., the 1100 and 5XXX series alloys.

Cathodic protection virtually eliminated the localized corrosion on all the aluminum alloys studied with the exception of 7178-T6 where it did not eliminate the edge corrosion. For example the mean depth of attack on 7079-T6 was reduced from over 15 mils to less than 1 mil. For 2024-T351, the mean attack was reduced from 40 mils to 3 mils, and for the alloy for which cathodic protection was least effective (7178-T6) all corrosion except for edge cracking was reduced to a maximum of 4 mils.

## ELECTRODE POTENTIALS

This phase of the investigation included the determination of the open circuit electrochemical potential of each specimen when immersed in quiescent sea water. Within the scope of this study it was not feasible to investigate the complex factors on which the electrochemical potentials of passive metals are dependent. For a detailed discussion of factors which affect the electrochemical potentials of film-pore type electrodes, the reader is referred to the papers by Akimov (9,10).

The electrochemical potential of each alloy (negative to a Ag/AgCl reference electrode) and the values reported by other investigators (8,11,12) are shown in Figs. 8-10. In addition to the maximum (most electropositive), minimum (most electronegative), and mean values of the observed potential of each unprotected specimen, the potential range observed on the cathodically protected specimen is also shown.

It will be noted that the potential values measured in this study are in most cases significantly electronegative to the values reported for sodium chloride solutions containing hydrogen peroxide (8) or those for highly aerated sea water flowing at 13 feet per second reported by LaQue (11). However, more recent data from INCO (12), also developed under velocity conditions, are in most instances more compatible with those data developed in the present study.

The potential data summarized in Table 2 are the mean values observed during the indicated time periods.

This table can be considered a galvanic series for the mean value open-circuit potentials of aluminum alloys in quiescent sea water. The potentials of an aluminum-5% zinc anode, a zinc anode (MIL-A-18001G), and a high potential proprietary aluminum anode have been added for reference purposes.

The mean open-circuit potential of aluminum alloys ranged from 0.69 volts to 1.24 volts negative to a Ag/AgCl reference electrode. It is evident that an initial potential difference of approximately 0.5 volt could exist if alloys from the two extremes of the table were coupled and immersed in sea water. Thus, accelerated corrosion is to be expected if certain combinations of aluminum alloys are electrically bonded in a marine structure.

Table 2 also shows that some of the structural aluminum alloys are more electronegative than the common galvanic anodes normally used in sea water. While this could present a serious problem, the more electronegative structural alloys in this study all demonstrated excellent corrosion resistance, and there was no indication that coupling these alloys to the aluminum alloy "anode" used in this experiment (minus 1.11 volts to Ag/AgCl) accelerated corrosion damage of the structural alloy. However, considerable caution should be used in coupling the more electronegative structural alloys to galvanic anode materials such as zinc (minus 1.05 volts) or aluminum-5% zinc (minus 0.95 volts).

## CORRELATION BETWEEN ELECTROCHEMICAL POTENTIAL AND CORROSION RESISTANCE

Analysis of the data showed that alloys with relatively electropositive potentials, i.e., minus 0.69 to 0.89 volts versus the Ag/AgCl reference electrode, were more susceptible to severe localized corrosion than alloys with more electronegative potentials. In Fig. 11 the mean depth of the five deepest pits is plotted as a function of the observed electrochemical potential. The marked correlation is readily evident.

The galvanic series for structural aluminum alloys in quiescent sea water (Table 2) has been divided into two

columns with the less electronegative alloys on the left. These alloys with potentials ranging from minus 0.69 to minus 0.89 volts suffered relatively severe localized corrosion and would not normally be suitable for use in sea water without cathodic protection or unless protected by a high quality coating.

In contrast, the alloys in the right-hand column, with potentials from minus 0.92 to minus 1.24 volts were essentially unattacked during the experiment. The Alcad 7178-T6 is an exception to the rule because it suffered edge cracking. In this case, however, the electrochemical potential determined was that of the cladding and not of the base metal. Considered in this light, the behavior of the Alclad 7178-T6 is more reasonably viewed as a failure of the cathodic protection provided by the electronegative cladding.

## SUMMARY AND CONCLUSIONS

The corrosion characteristics of the aluminum alloys studied varied widely but the behavior can be conveniently summarized by classifying the alloys by the observed electrochemical potential. The more electronegative alloys (minus 0.92 to minus 1.24 volts to the Ag/AgCl reference) were inherently resistant to both surface pitting and crevice corrosion.

Alloys less electronegative than minus 0.89 volts suffered severe corrosion. In general, the severity of the corrosion problem increased for the more electropositive (less electronegative) alloys. Alloys in this group should not be used in sea water without some form of supplementary protection.

Cathodic protection either from an external aluminum anode or from Alcladding was effective in reducing the surface pitting and crevice corrosion of the alloys studied to tolerable limits. However, while cathodic protection eliminated the edge cracking observed on unprotected X7002-T6 alloy, it did not completely eliminate this phenomena in the 7178-T6 alloy.

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Table 1

Aluminum Alloys - Depth of Attack (mils)
After 368 Days Exposure in Sea Water, Key West, Florida

| Alloy Designation and Temper | Depth of Attack (mils)[1] | |
|---|---|---|
| | No Cathodic Protection | With Cathodic Protection[2] |
| 5052-H32; 5083-0; 5086-H32; H34, H112 5257-H25; 5456-H321 6061-T651; X7005-T63 7106-T63 | <1 | <1 |
| 1100-H14; 5050-H34; 5052-H34; 5154-H38; Alc. X7002-T6; Alc. 7178-T6[4] | 1-4 | 1 mil except: 1100-H14 (2 mils), and Alc. 7178-T6 (4 mils)[4] |
| 1100-F; 2014-T6; 6061-T6; X7002-T6[3]; | 5-10 | 1 mil or less except; 2014-T6 (2 mils) |
| 3003-H14; 7079-T6; 7075-T7351 | 11-20 | 1 mil or less |
| 2024-T351; 2219-T87; 7178-T6[3] | 25-40 | 3 mils or less 7178-T6[3] |

NOTES: 1. Based on average of 5 deepest penetrations.
2. Aluminum anode used.
3. Edges cracked severely.
4. Edges cracked.

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Table 2

## ALUMINUM ALLOYS

Potentials in Quiescent Sea Water - Key West, Florida
63 Days Exposure (Except as Noted Below)

| Alloy Designation and Temper | Mean Electrode Potential in Volts (Neg. Ag/AgCl Ref.) | Alloy Designation and Temper | Mean Electrode Potential in Volts (Neg. Ag/AgCl Ref.) |
|---|---|---|---|
| 2024-T351; 2219-T87 | 0.69-0.70 | 7106-T63; 6061-T651; 5086-H112; 5050-H34; 1100-H14; 5083-0 | 0.92-0.94 |
| 7178-T6; X7002-T6; 7075-T7351; 7079-T6; 2014-T6 | 0.73-0.79 | Al Anode (5% Zn) | 0.95 |
| | | 5456-H321; 5086-H32; 5086-H34; Alc. 7178-T6; X7005-T63; Alc. X7002-T6; 5052-H34; 5052-H32 | 0.96-0.98<br>1.01-1.02 |
| 1100-F; 3003-H14; 6061-T6 | 0.88-0.89 | Zinc Anode (MIL-A-18001G); 5154-H38 | 1.05 |
| | | Al Anode (proprietary) | 1.11 |
| | | 5257-H25 | 1.24 |

Alloys whose potentials were observed for longer than 63 days:

| Alloy | Number Days Exposed |
|---|---|
| 2014-T6 | 328 |
| 5086-H34 | 125 |
| 5456-H321 | 328 |
| 6061-T6 | 360 |
| Alc. 7178-T6 | 168 |
| Al Anode (Proprietary) | 360 |

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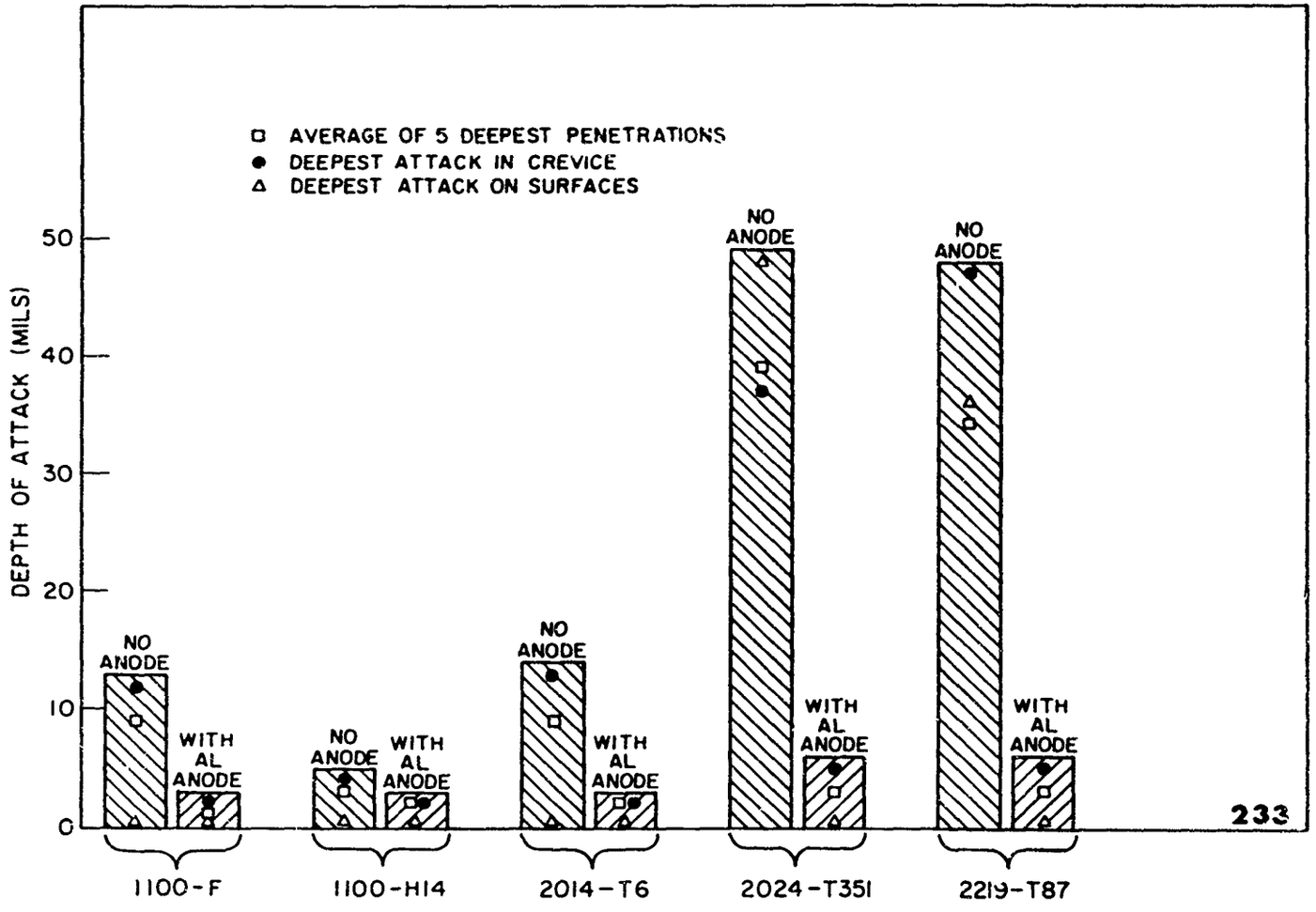


Fig. 1 - 1XXX and 2XXX series aluminum alloys: corrosion and effect of cathodic protection. 368-day sea water exposure, Key West, Florida.

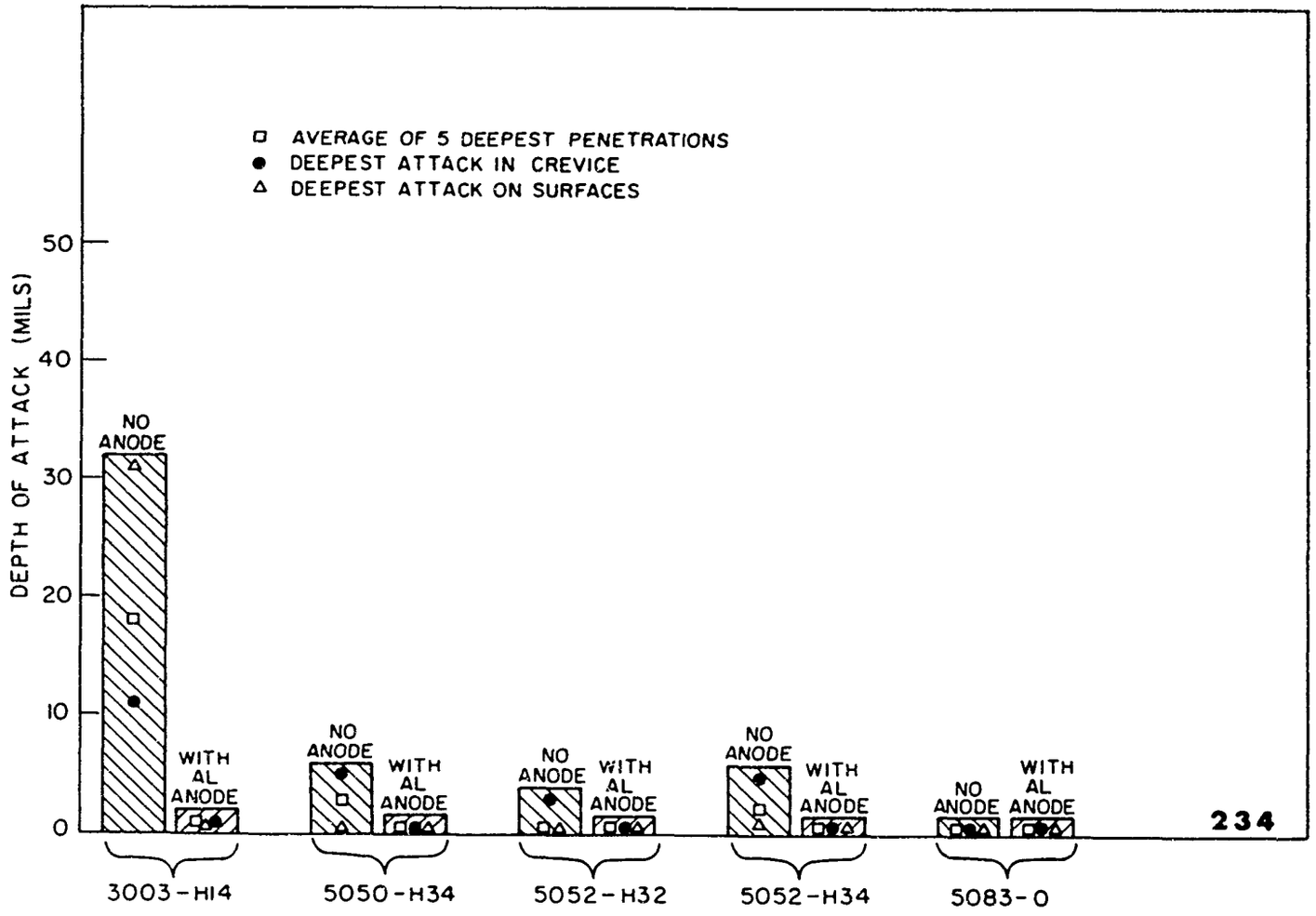


Fig. 2 - 3XXX and 5XXX series aluminum alloys: corrosion and effect of cathodic protection. 368-day sea water exposure, Key West, Florida.

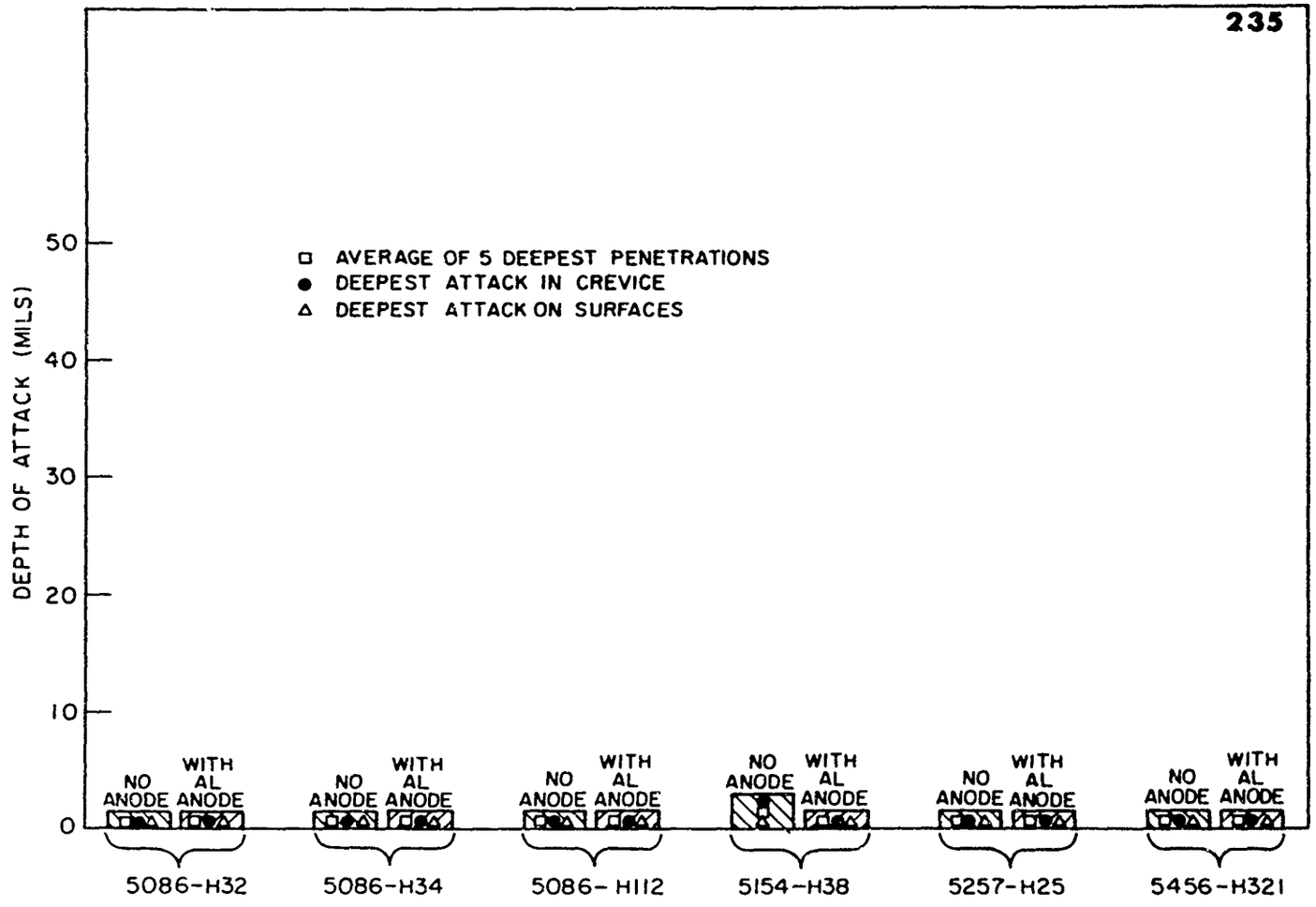


Fig. 3 - 5XXX series aluminum alloys: corrosion and effect of cathodic protection. 368-day sea water exposure, Key West, Florida.

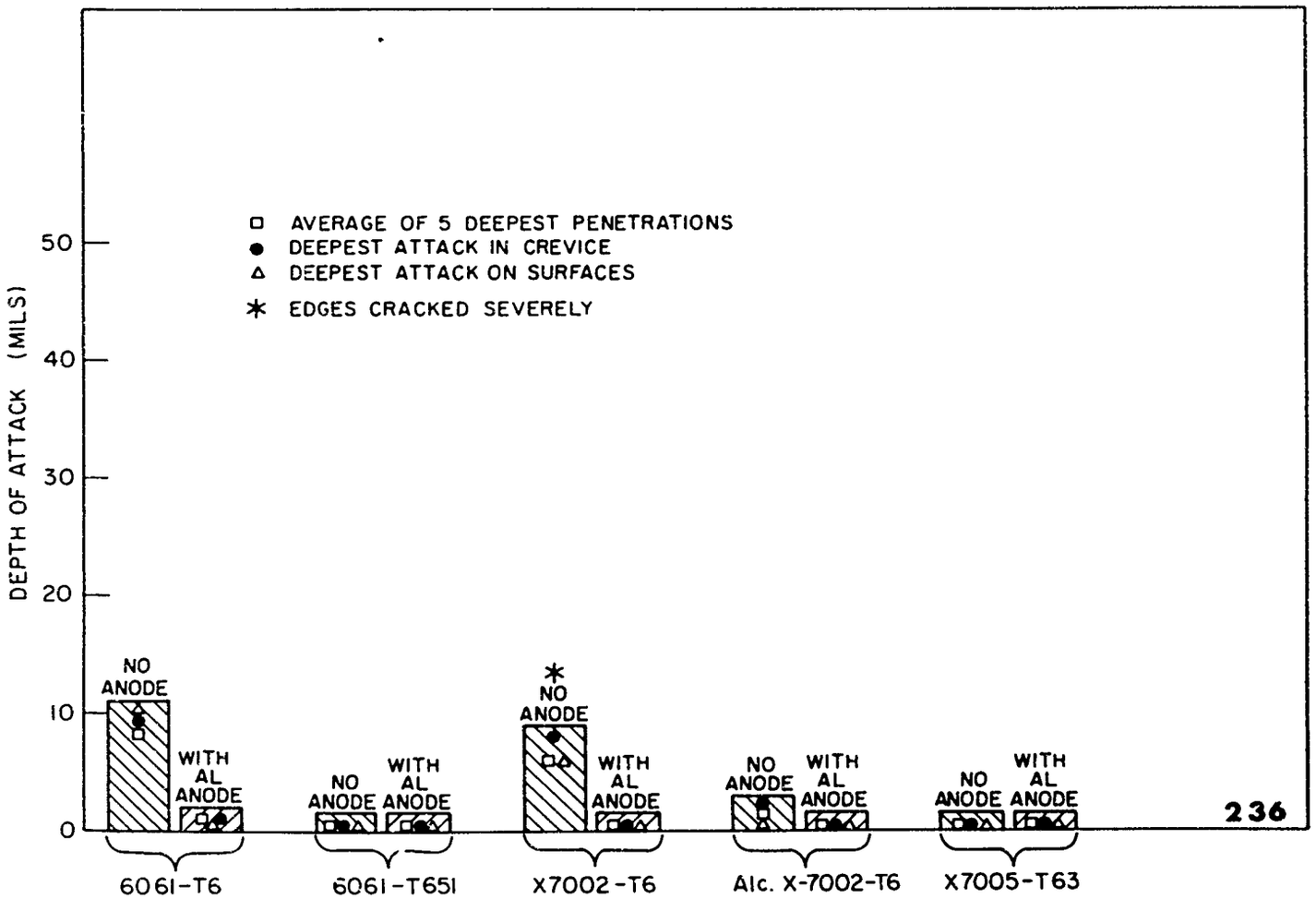


Fig. 4 - 6XXX and 7XXX series aluminum alloys: corrosion and effect of cathodic protection. 368-day sea water exposure, Key West, Florida.

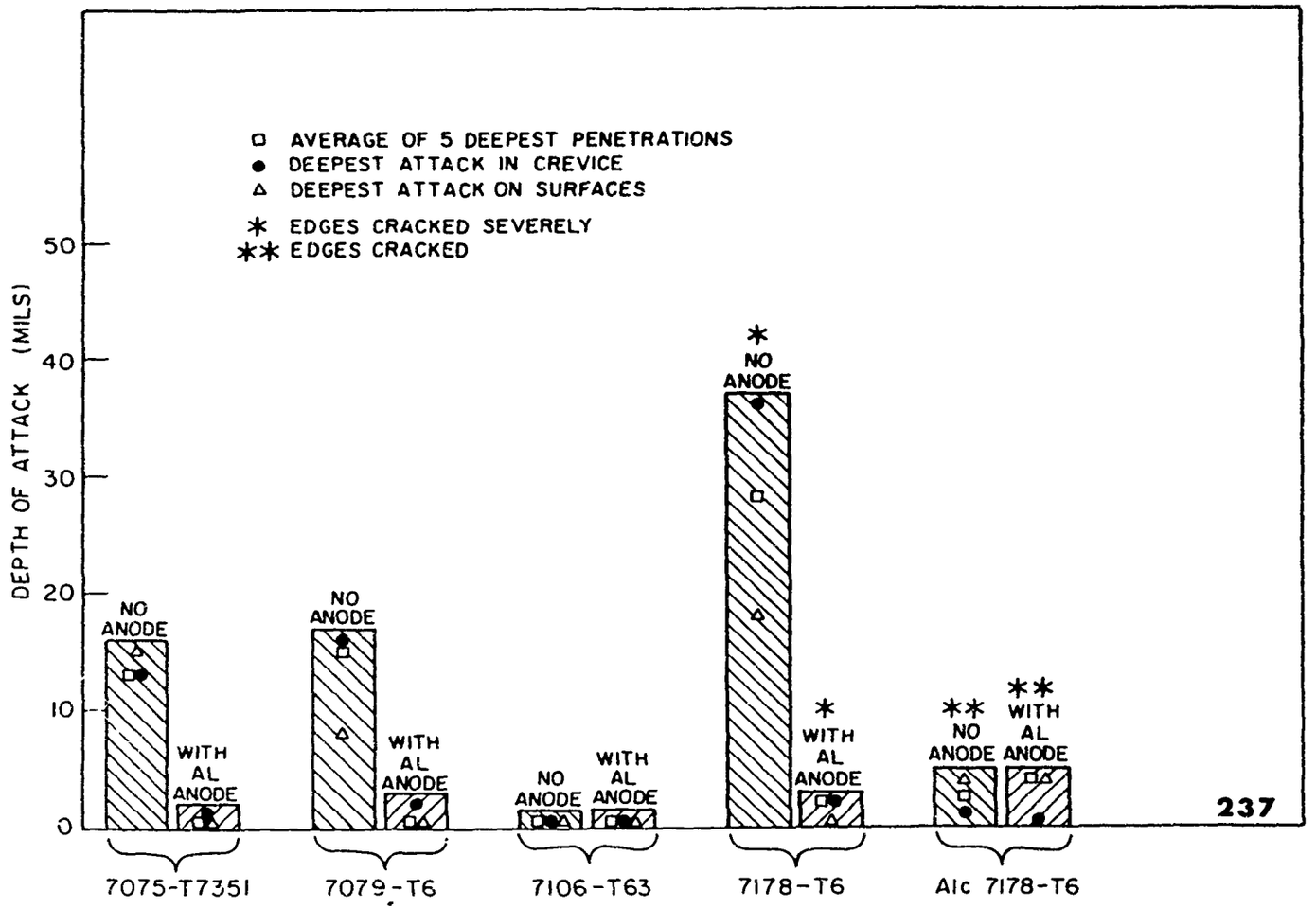


Fig. 5 - 7XXX series aluminum alloys: corrosion and effect of cathodic protection. 368-day sea water exposure, Key West, Florida.

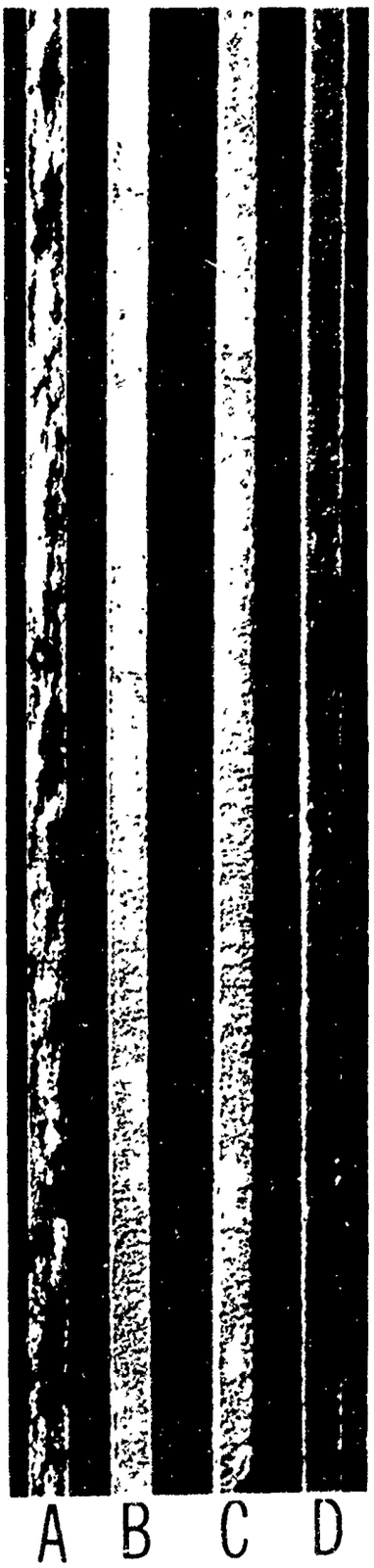


Fig. 6 - Edge cracking (delamination) of X7002-T6 aluminum alloy showing the effectiveness of Alclad and cathodic protection: (A) X7002-T6, (B) X7002-T6 with Cathodic Protection, (C) Alclad X7002-T6, (D) Alclad X7002-T6 with Cathodic Protection.


Fig. 7 - Edge cracking (delamination) of 7178-T6 aluminum alloy showing the ineffectiveness of Alclad and cathodic protection: (A) 7178-T6, (B) 7178-T6 with Cathodic Protection, (C) Alclad 7178-T6, (D) Alclad 7178-T6 with Cathodic Protection.

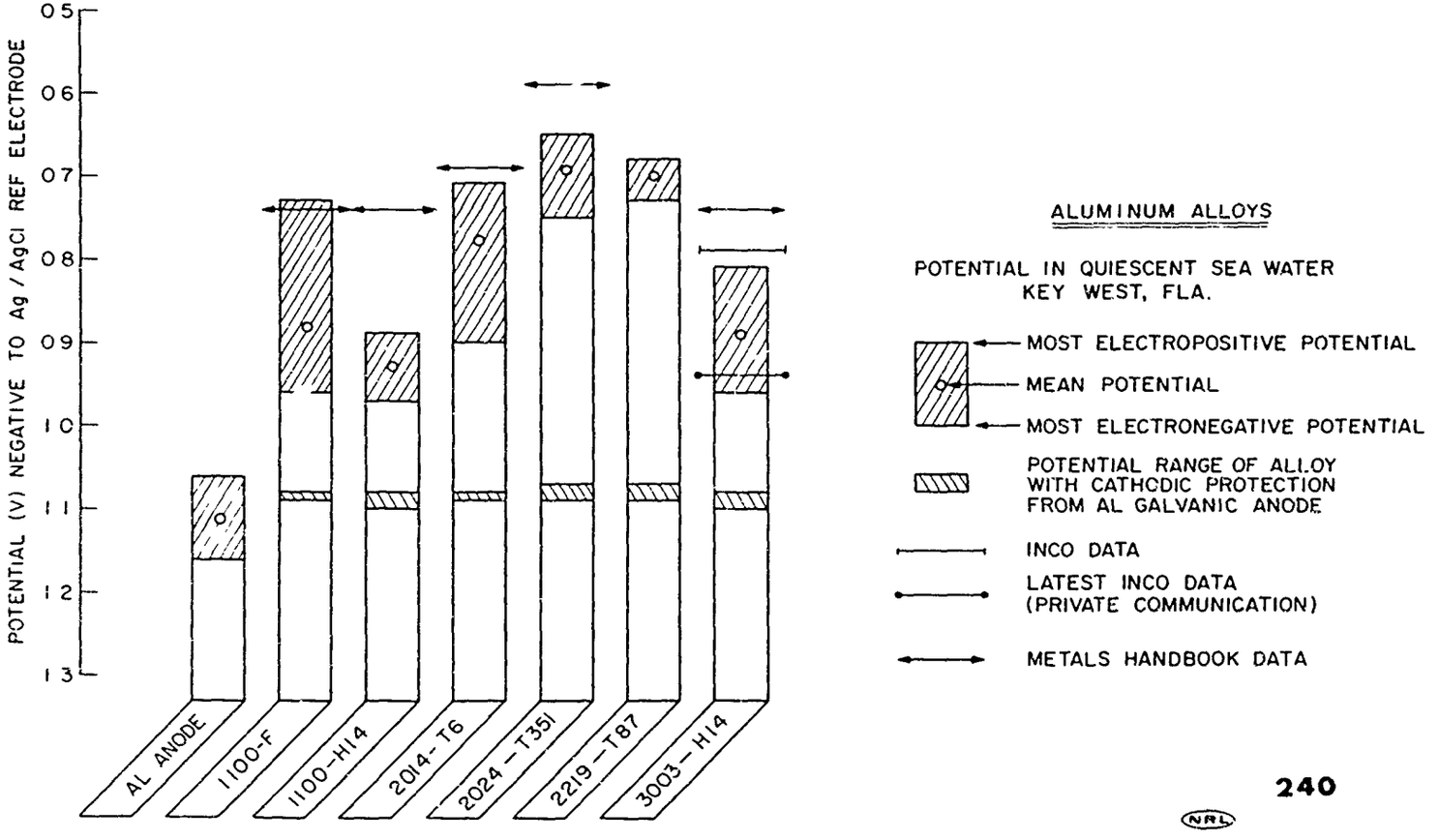


Fig. 8 - Aluminum alloys: electrode potentials determined by NRL in quiescent sea water during exposure at Key West, Florida, compared to values from other sources.

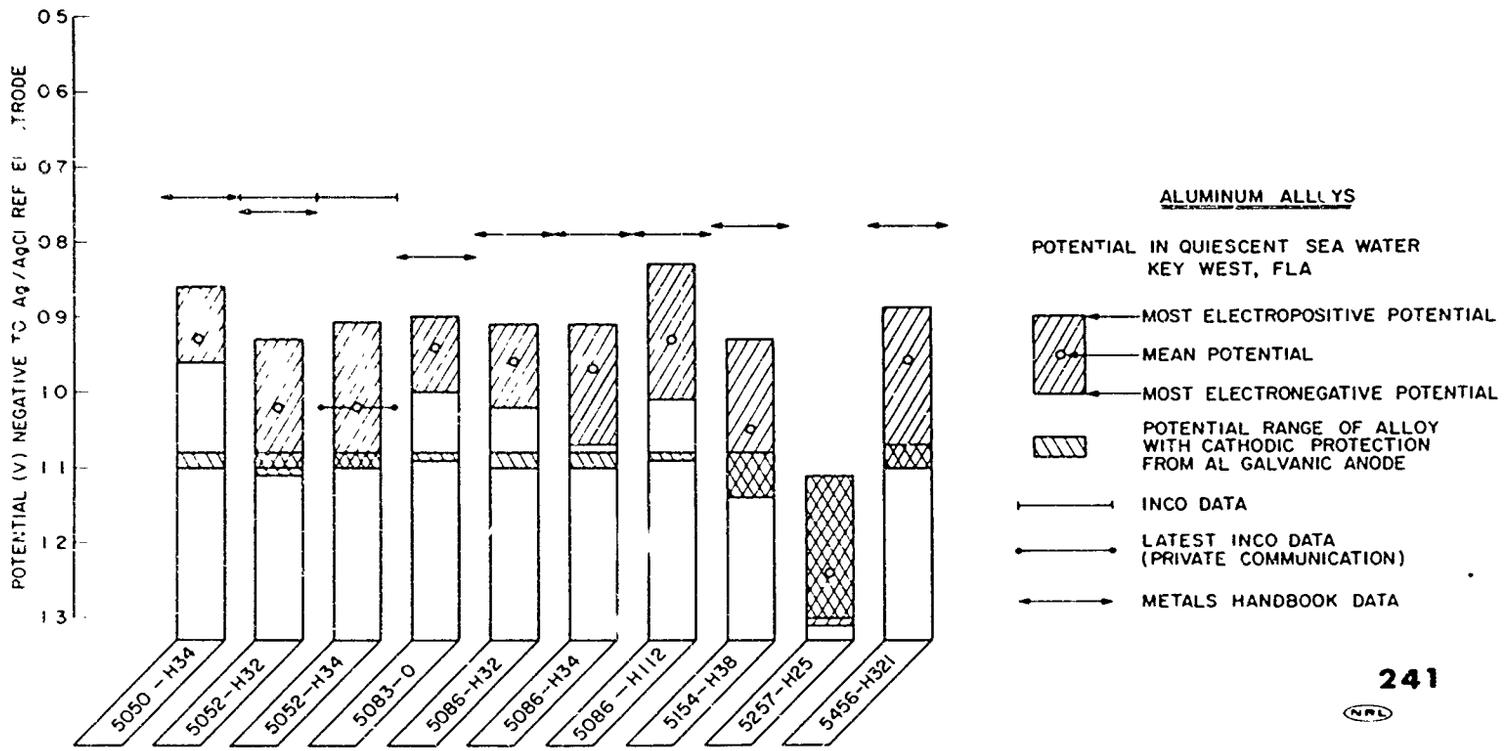


Fig. 9 - Aluminum alloys: electrode potentials determined by NRL in quiescent sea water during exposure at Key West, Florida, compared to values from other sources.

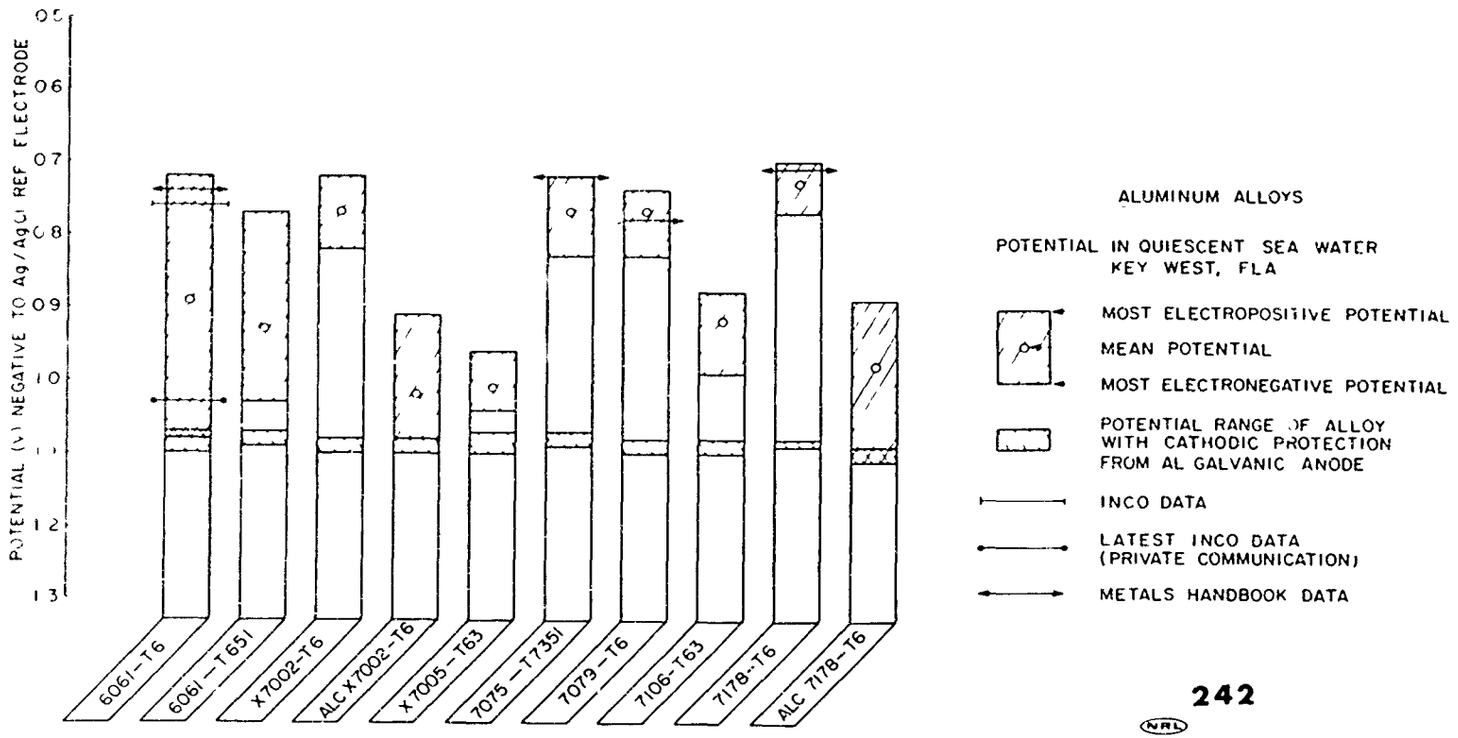


Fig. 10 - Aluminum alloys: electrode potentials determined by NRL in quiescent sea water during exposure at Key West, Florida, compared to values from other sources.

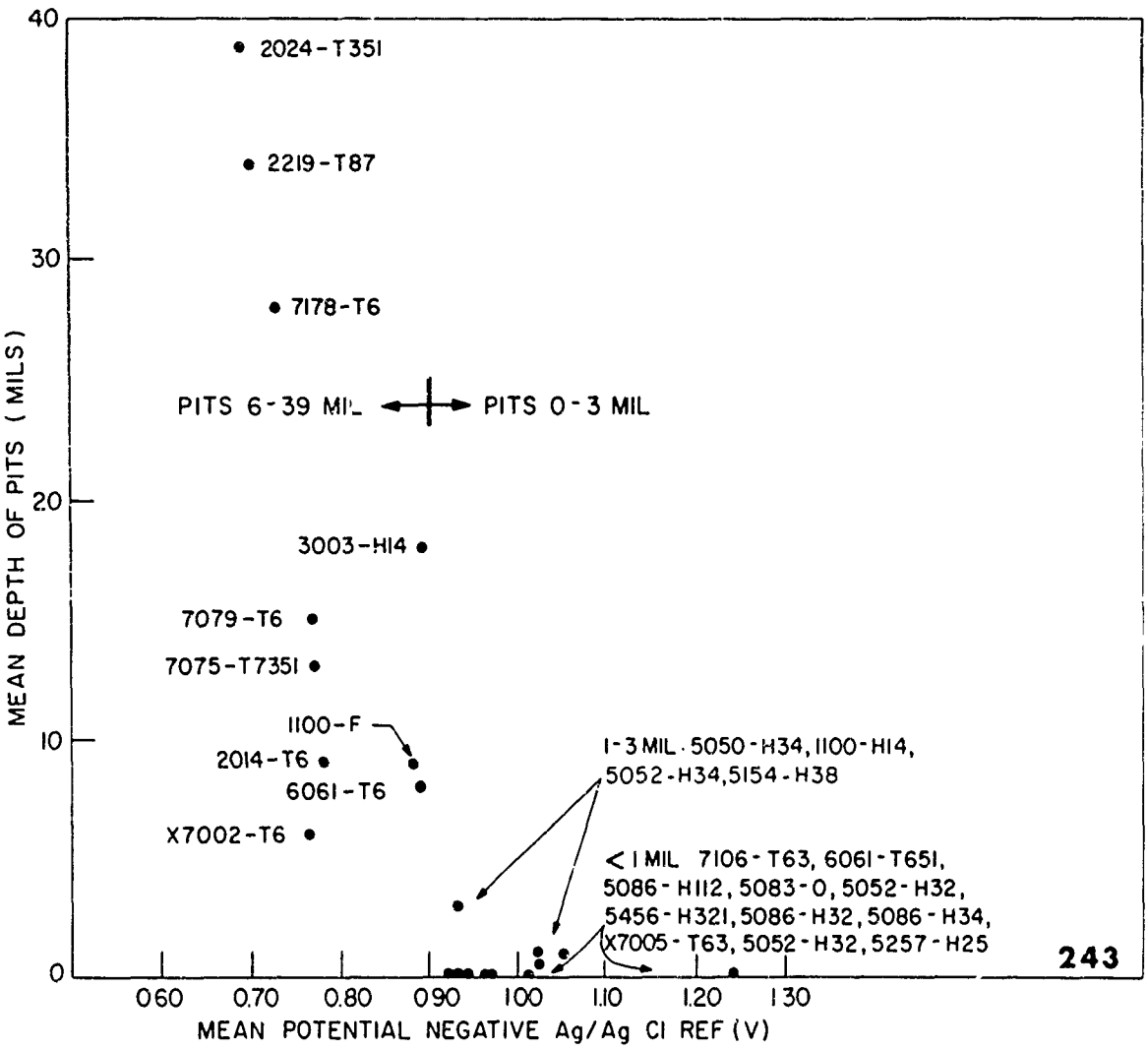


Fig. 11 - Aluminum alloys: pitting characteristics vs. electrode potentials in sea water at Key West, Florida.

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13 ABSTRACT

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