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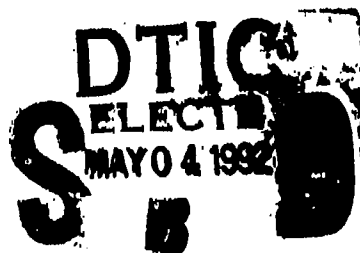
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CORROSION OF HIGH DENSITY KINETIC ENERGY PENETRATOR MATERIALS

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METALS RESEARCH BRANCH

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ABSTRACT

The corrosion behavior of DU-3/4% Ti and DU-2% Mo alloys was assessed by electrochemical polarization techniques and exposure to both 5% salt fog at 35°C and a 95% relative humidity at 45°C. The efficacy of an ion vapor deposited aluminum coating in mitigating the corrosion of these alloys was also assessed.

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INTRODUCTION

High density depleted uranium (DU) alloys possess superior armor piercing capabilities and ballistic properties for artillery applications involving penetrators. These alloys are currently in use by the United States and the United Kingdom for the above application. A joint parallel investigation of the corrosion behavior of high density DU and tungsten alloys has been conducted by the United States, the United Kingdom, and Australia under a technical cooperation agreement (TTCP).¹ The U.S. Army Materials Technology Laboratory (MTL) was the lead laboratory in this cooperative program. This report covers the work on DU alloys carried out at MTL only.

The objective of the program was to conduct a comparative corrosion evaluation of the United States M774 U-3/4% Ti bars processed by Nuclear Metals, Inc. (NMI) and the United Kingdom U-2% Mo bars provided by Dr. Simon Anthony of the Atomic Weapons Research Establishment.

EXPERIMENTAL PROCEDURE

Materials

A summary of the source, processing procedure, heat treatment, chemistry, and mechanical properties are listed in Table 1 for the DU-3/4% Ti alloy and in Table 2 for the DU-2% Mo alloy.

Table 1. U.S.A. DU-3/4% TI PROCESSING, HEAT TREATMENT, CHEMISTRY, AND MECHANICAL PROPERTIES

U.S.A. DU-3/4% TI M774 Nuclear Metals Bars	
Heat Treatment	
• Solution treated at 850°C (1562°F) in vacuum for two hours • Vertically water quenched at 18 in. (0.46 mm) per minute • Aged 355°C (671°F) for 16 hours in helium gas recirculating furnace	
Chemistry	
• 0.73% Ti; 55 ppm C, 20 ppm Fe, 8 ppm Ni, 4 ppm Cu, 60 ppm Si, 0.6 ppm H	
Mechanical Properties	
• Y.S. 113.7 Ksi • U.T.S. 204.5 Ksi • Elong. 2.5% • K_Q 31.1 Ksi $\sqrt{\text{in}}$ at -46°C (-50°F)	

1. Levy, M., et al. *Final Report on TTCP Operating Assignment on Corrosion of High Density Penetrator Materials*. Subgroup P, U.S. Army Materials Technology Laboratory, Technical Panel/Metals, PTP, January 2, 1988.

Table 2. U.K. DU-2% Mo PROCESSING, HEAT TREATMENT, CHEMISTRY, AND MECHANICAL PROPERTIES

U.K. DU-2% Mo Produced by Coreduction at British Nuclear Fuel Limited Springfield Laboratory; Vacuum Remelted at Aldermaston; Gamma Phase* Extruded at Teddington.

Heat Treatment

- Solution treated at 800°C (1472°F) in vacuum for three hours
- Fast helium gas cooled
- Aged 500°C (932°F) in vacuum for two hours

Chemistry

- 2.05 - 2.20% Mo; 14 - 53 ppm C, 30 - 35 ppm Fe, 15 - 25 ppm Ni, 15 - 40 ppm Cu, 10 ppm Si, 10 - 20 ppm Al, 10 - 15 ppm Mn, 10 ppm Mg, 10 ppm Cr

Mechanical Properties

- Y.S. 105 Ksi
- U.T.S. 165 Ksi
- Elong. 10%
- Hardness - HRC 33

*Soft body-centered cubic structure at temperatures above 770°C.

Test Specimens and Procedures

Various test specimens were fabricated for electrochemical potentiodynamic polarization, humidity, and salt fog corrosion evaluations.

The specimens for potentiodynamic polarization were 0.625 in. (15.88 mm) in diameter and 0.125 in. (3.175 mm) in thickness. The reference electrode was a saturated calomel electrode (SCE) separated by a glass bridge with a vycor tip. The working electrode surface area (DU alloy) was 1.0 cm². A standard electrochemical polarization cell containing 600 ml of argon-saturated solution was used in conjunction with a Princeton Applied Research Laboratories Corrosion Measurement Console Model 350 to make the measurements. In order to describe the anodic and cathodic processes, anodic and cathodic polarization measurements were made utilizing the potential sweep method of potentiostatic polarization. The electrode potential was continuously changed at a constant rate of 5000 mV/hr and current simultaneously recorded. Corrosion rates in mils per year were determined by extrapolation of the cathodic portion of the polarization curve to the corrosion potential. Anodic polarization measurements and reverse polarization scans were performed to

determine the occurrence of dissolution, passivation, or pitting. One hour potential-time data were obtained for all alloys in all environments to determine the corrosion potentials. The environments included aqueous solutions containing, respectively: 50 ppm NaCl, 3.5% NaCl, 1.0 N HCl, 2.0 N HCl, 2.5 N HCl, 3.0 N HCl, 5.0 N HCl, or 1.0 N H₂SO₄.

For the salt fog and humidity tests, eight U-3/4% Ti and eight U-2% Mo disc specimens were fabricated at 1.189 in. and 1.062 in. (30.20 mm and 26.97 mm) in diameter, respectively, and 0.125 in. (3.175 mm) thick. The four aluminum ion vapor deposited (Al IVD) DU alloy discs were 1.193 in. (30.30 mm) in diameter and 0.125 in. (3.175 mm) thick. The Al IVD coating thickness was 1.0 mil.

The aluminum was ion vapor deposited on the depleted uranium specimens at McDonnell Douglas Company in St. Louis. This Al coating had a minimum purity of 99%. Coated specimens were given a 60-second immersion in Alodine 1200 chromate conversion solution to impart additional protection against salt spray. The coating conformed to the requirements of military specification MIL-C-83488B, Class 1, Type II.

Four uncoated U-3/4% Ti and four uncoated U-2% Mo specimens were exposed to a 5% salt fog environment at 35°C (ASTM B 117-73) for a period of 23 days. After 6, 12, 19, and 23 days of exposure, corrosion products were removed by immersion in 20% nitric acid for two minutes and the specimens were weighed. Corrosion rates were computed using the weight loss data.

The other remaining four uncoated U-3/4% Ti and four uncoated U-2% Mo specimens were exposed to a 95% relative humidity at 45°C environment for 40 days of exposure. After 8, 18, 29, and 40 days of exposure, corrosion products were removed by immersion for two minutes in 20% nitric acid. The specimens were weighed and weight loss or gain data was used to compute corrosion rates.

Two Al coated U-3/4% Ti and two Al coated U-2% Mo specimens were exposed to a 5% salt fog environment at 35°C, in accordance with MIL-C-83488B, Class 1, Type II, for a period of 28 days. After 6, 12, 19, 23, and 28 days of exposure, loose corrosion products were removed by rinsing with distilled water. Specimens were weighed, weight losses or gains were recorded, and corrosion rates were computed. The test procedure described above is summarized in Table 3.

Table 3. TEST PROCEDURE

Positioning of Specimens During Exposure

- Tilted at approximately a 60° angle to the horizontal against an L-shaped fiberglass holder
- Rinsed with water and turned over every 24 hours to ensure equal exposure to both flat surfaces

Removal of Oxide and Corrosion Debris

- Uncoated Specimens Immersed in 20% HNO₃ for two minutes, rinsed with distilled water, and air dried
- Coated Specimens Rinsed with distilled water and air dried

Determining the Effect of Exposure

- After removal of corrosion debris, specimens were reweighed
- Rate of corrosion was determined from weight change averaged for the replicates

RESULTS AND DISCUSSION

Potentiodynamic Polarization

Polarization curves were obtained for U-3/4% Ti and U-2% Mo alloys in the following solutions, respectively: 50 ppm and 3.5% sodium chloride; 1.0 N HCl; 2.0 N HCl; 2.5 N HCl; 3.0 N HCl; 5.0 N HCl; 1.0 M NaOH; and 1.0 N H₂SO₄ solutions.

Figure 1 shows that the U-2% Mo curve was displaced to more active potentials in 50 ppm NaCl solutions when compared to the U-3/4% Ti curve. Both curves were similar in shape and exhibited similar corrosion rates. The reverse scans indicated pitting had occurred at ~ 0.100 V. Visual observations confirmed the presence of pits. In Figure 2, at the higher 3.5% sodium chloride concentration, the curves for U-3/4% Ti and U-2% Mo overlapped and the corrosion rates again were similar. Increasing either the Cl concentration or the solution temperature served to increase corrosion rates, and to shift the corrosion potential in the more active direction, as shown in Figures 1 through 3, and Table 4.

Figure 4 compares the cathodic polarization curves for U-3/4% Ti and U-2% Mo in 1.0 N HCl. At equi-potentials, current densities were greater for the U-2% Mo alloy. Figure 5 shows that increasing the HCl concentration increases the cathodic current density for the U-3/4% Ti alloys indicative of increasing corrosion rates. Polarization curves for U-3/4% Ti and U-2% Mo alloys in 1.0 M NaOH are shown in Figure 6. Both alloys exhibit an active passive transition, but the U-3/4% Ti has a more noble corrosion potential and a more extensive and stable passive region in the 1.0 M NaOH solution. Similar results were obtained for as-cast DU-Ti and DU-Mo alloys in an earlier study.² In 1.0 N H₂SO₄ solution, both alloys exhibit similar polarization curves and corrosion rates, as shown in Figure 7. At +0.3 V any protective film formed breaks down and active corrosion occurs.

2. Levy, M., and Zabielski, C. *Electrochemical Behavior of Some Binary and Polynary Uranium Alloys*, Physical Metallurgy of Uranium Alloys. Brook-Hill Publishing Co., Chestnut Hill, Massachusetts, 1976, p. 897-947.

Salt Fog and Humidity Tests

Figure 8 plots weight losses in mg/cm^2 versus days exposure for U-3/4% Ti and U-2% Mo disc specimens in 5% salt fog environment. The weight loss data for the U-3/4% Ti and U-2% Mo disc specimens were very similar. After a 23-day exposure, the weight loss per cm^2 was $\sim 600 \text{ mg}/\text{cm}^2$ for both alloys. Figure 9 shows the corrosion rates in mils per year versus days exposure for both alloys. At the end of 23 days exposure, the corrosion rate was $\sim 190 \text{ mpy}$ for both alloys.

After 40 days of exposure at 45°C and 95% relative humidity, the weight losses and corrosion rates for U-2% Mo alloys were $0.30 \text{ mg}/\text{cm}^2$ and $0.047 \text{ mils per year}$, and for U-3/4% Ti alloys, were $0.15 \text{ mg}/\text{cm}^2$ and $0.02 \text{ mils per year}$. Comparing the corrosion rates in the two environments, it is clear that the 5% NaCl salt fog environment is ~ 3800 times more severe than the 95% RH environments.

Figure 10 compares U-3/4% Ti and U-2% Mo disc specimens before and after cleaning in 20% nitric acid after six days exposure to the 5% salt fog environment. Although corrosion rates based upon weight loss are similar ($\sim 100 \text{ mpy}$), the U-2% Mo alloy appears to be more severely pitted. Figure 11 shows cleaned disc specimens after 12 days exposure to 5% salt fog environment. Three of the four U-3/4% Ti disc specimens cracked approximately in half because of residual stresses. The cracks appeared to initiate near the center of the discs because the maximum tensile stresses were present in the center of the bar after the vertical water quenching operation and were only partially relieved by aging. Figure 12 shows cleaned discs after 16 days of exposure. Pitting is more severe on both alloys, but the U-2% Mo alloys show the most severe attack on the surface, as well as at the edges. Figure 13 shows cleaned U-3/4% Ti and U-2% Mo disc specimens after 23 days of exposure. In addition to pitting, preferential attack at the edges is greater, particularly for the U-2% Mo alloy.

Figure 14 shows the two cleaned Al IVD coated U-3/4% Ti and U-2% Mo discs after six days exposure in 5% salt fog environment. Prior to completion of the six day test period, daily visual examination showed evidence of pinpoint corrosion of DU-3/4% Ti alloy after one day, indicative of pinholes in the original coating. The Al IVD coated U-2% Mo alloy displayed pinhole corrosion after five days of testing. Blistering of the Al IVD coating was evident on the U-2% Mo discs after six days of exposure. Figure 15 shows that after 12 days exposure to the 5% salt fog environment, pits in the Al IVD coating on the DU-3/4% Ti alloy had enlarged and more widespread blistering of the coating on DU-2% Mo alloy had occurred. Figure 16 shows that after 19 days of exposure to 5% salt fog, the pits in the Al IVD coating of the U-3/4% Ti discs underwent further enlargement and corrosion of the underlying U-2% Mo alloy (black corrosion product) was observed. The underlying DU-2% Mo alloy appeared to have more visible corrosion than the DU-3/4% Ti alloy. As exposure time increased to 23 and 28 days, as shown in Figures 17 and 18, the amount of visible corrosion of underlying alloy increased, particularly for the U-2% Mo alloy. After 28 days exposure to 5% salt fog environment, the average weight loss for the two Al IVD coated U-3/4% Ti discs was $0.32 \text{ mg}/\text{cm}^2$, and for the two Al IVD coated U-2% Mo discs the larger average weight gain of $1.62 \text{ mg}/\text{cm}^2$ was due to the formation of more corrosion products.

SUMMARY

The corrosion data are summarized in Table 4. Potentiodynamic polarization scans disclosed that pitting of both alloys occurs in 50 ppm and 3.5% NaCl solutions, but corrosion rates are less than 1.0 mil per year. The corrosion rate for the U-2% Mo alloy is significantly higher than the U-3/4% Ti alloy in both HCl and NaOH solutions. The corrosion rate for both alloys is well below 1.0 mil per year in 1.0 N H₂SO₄ solution.

Table 4. CORROSION RATES FOR UNCOATED AND COATED* U-3/4% TI (STA) AND U-2% Mo SPECIMENS

A. Uncoated Specimens		
Environment	Corrosion Rate ¹ (MPY)	
	U-3/4% Ti	U-2% Mo
50 ppm NaCl	0.04	0.07
3.5% NaCl	0.26	0.33
1.0 N HCl	8.10	339.70
2.0 N HCl	34.50	—
2.5 N HCl	410.00	—
3.0 N HCl	534.00	—
5.0 N HCl	1983.00	—
1.0 M NaOH	1.16	6.10
1.0 N H ₂ SO ₄	0.14	0.06
Environment	Corrosion Rate ² (MPY)	
	U-3/4% Ti	U-2% Mo
5% Salt Fog (23-Day Exposure)	188.60	188.00
95% Humidity (40-Day Exposure)	0.02	0.05
B. Coated Specimens*		
Environment	Corrosion Rate ³ (MPY)	
	U-3/4% Ti	U-2% Mo
5% Salt Fog (28-Day Exposure)	0.09	+0.43

*Al IVD Coating, 1 mil thick

1 Determined from potentiodynamic polarization

2 Determined from weight loss

3 Determined from weight change (+ denotes a weight gain)

Exposure to 5% salt fog at 35°C caused very high corrosion rates comparable for both alloys. Pitting occurred over the entire cross section and appreciable corrosion occurred on the edges. Cracking occurred across the center of the majority of the U-3/4% Ti discs because of the presence of residual stresses.

Very low corrosion rates were noted for the DU-3/4% Ti and DU-2% Mo alloys exposed to a 95% RH environment at 45°C (0.020 and 0.047 mils per year, respectively). The 5% salt fog environment accelerated corrosion by a factor of more than 3000.

Corrosion rates for the Al IVD coated U-3/4% Ti and U-2% Mo specimens after 28 days exposure to 5% salt fog at 35°C were very small when compared with uncoated specimens in the same environment. In the case of the coated alloys, it should be noted that most corrosion products could not be removed by rinsing with distilled H₂O. As a consequence, corrosion rates which are based upon weight loss or gain are not valid in this case. Corrosion of the underlying alloys occurred due to pinhole defects in the coating. Severe blistering of the coating on the DU-2% Mo alloy was observed and was probably due to moisture penetration and follow-on corrosion of the substrate. The accelerated corrosion tests performed on DU alloys coated with Al IVD demonstrated a substantial improvement in corrosion resistance of these alloys, but formation of defect or pinhole-free coating would be highly desirable if the useful shelf life of coated DU parts is to be extended.

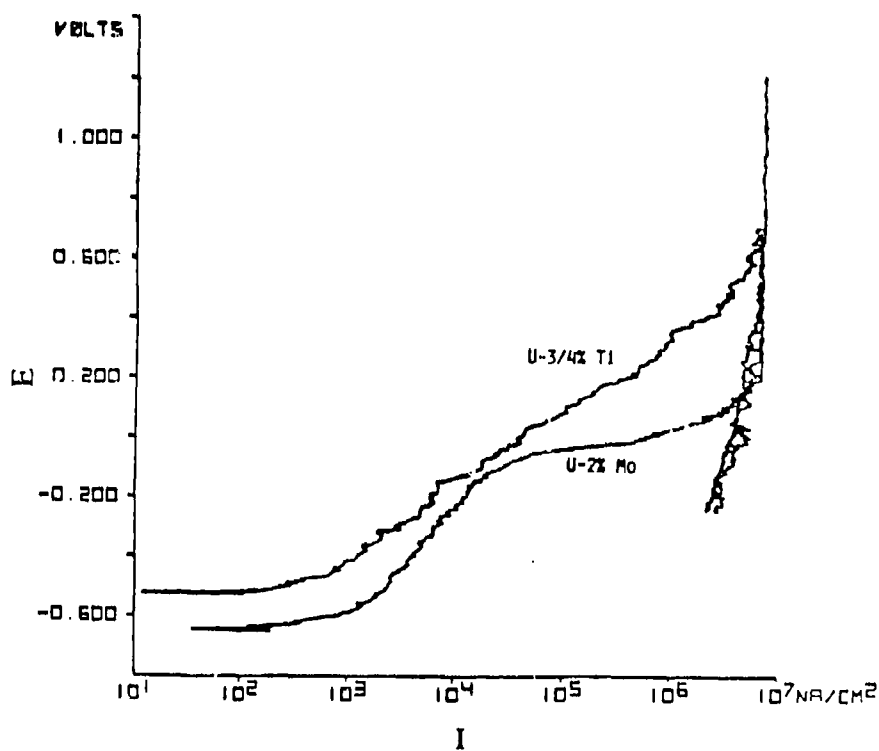


Figure 1. Anodic potentiodynamic polarization curves for U-3/4% Ti and U-2% Mo alloys in 50 ppm sodium chloride solution at 25°C. Scan rate 1.388 mV/sec.

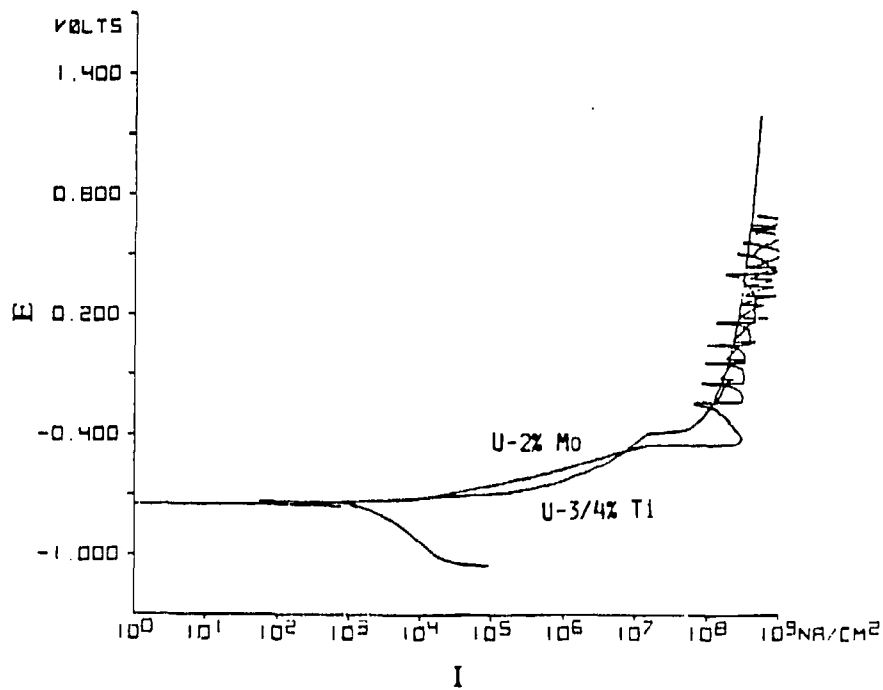


Figure 2. Potentiodynamic polarization curves for U-3/4% Ti and U-2% Mo alloys in 3.5% sodium chloride solutions at 25°C. Scan rate 1.388 mV/sec.

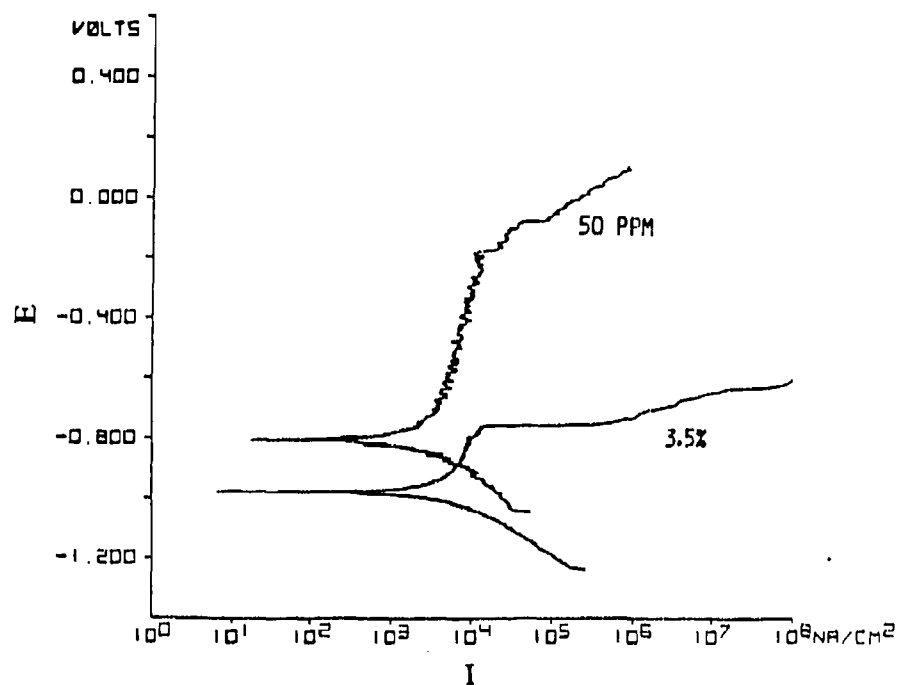


Figure 3. Potentiodynamic polarization curves for U-3/4% Ti in sodium chloride solutions at 65°C. Scan rate 1.388 mV/sec.

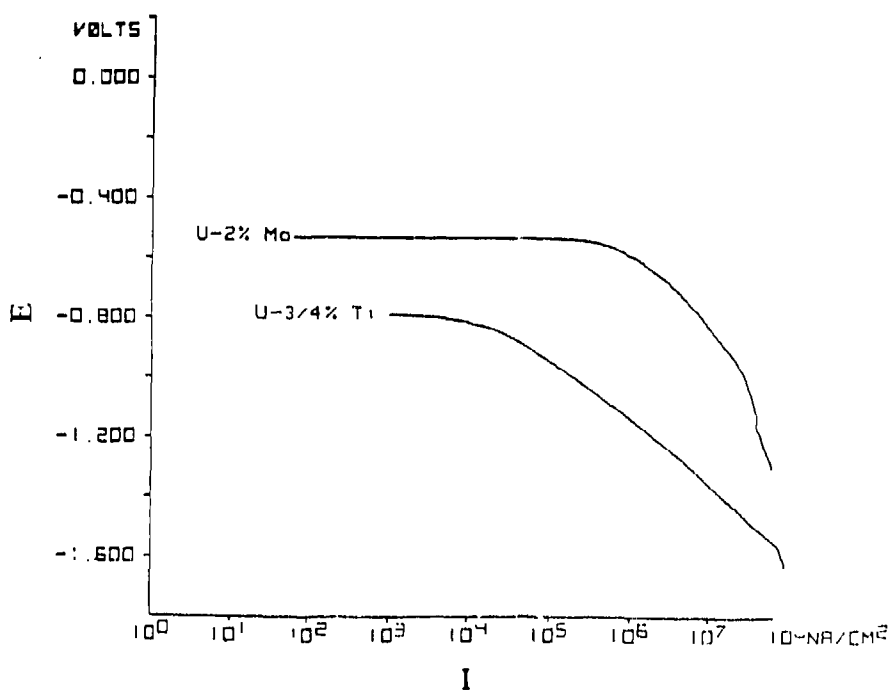


Figure 4. Cathodic potentiodynamic polarization curves for U-3/4% Ti STA and U-2% Mo in 1.0 N HCl at 25°C. Scan rate 1.388 mV/sec.

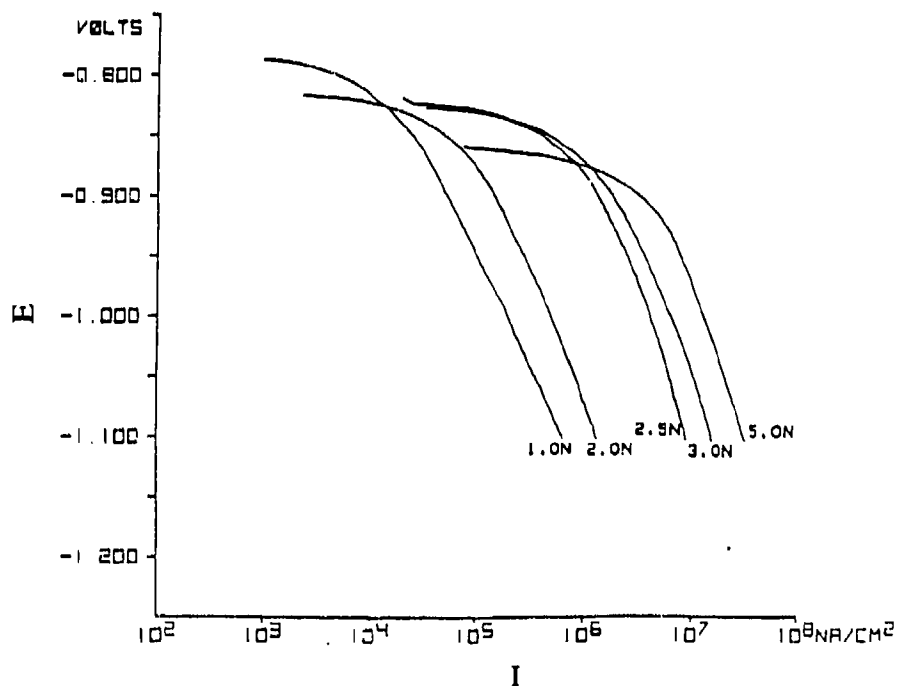


Figure 5. Effect of HCl concentration on cathodic potentiodynamic polarization of U-3/4% Ti STA at 25°C. Scan rate 1.388 mV/sec.

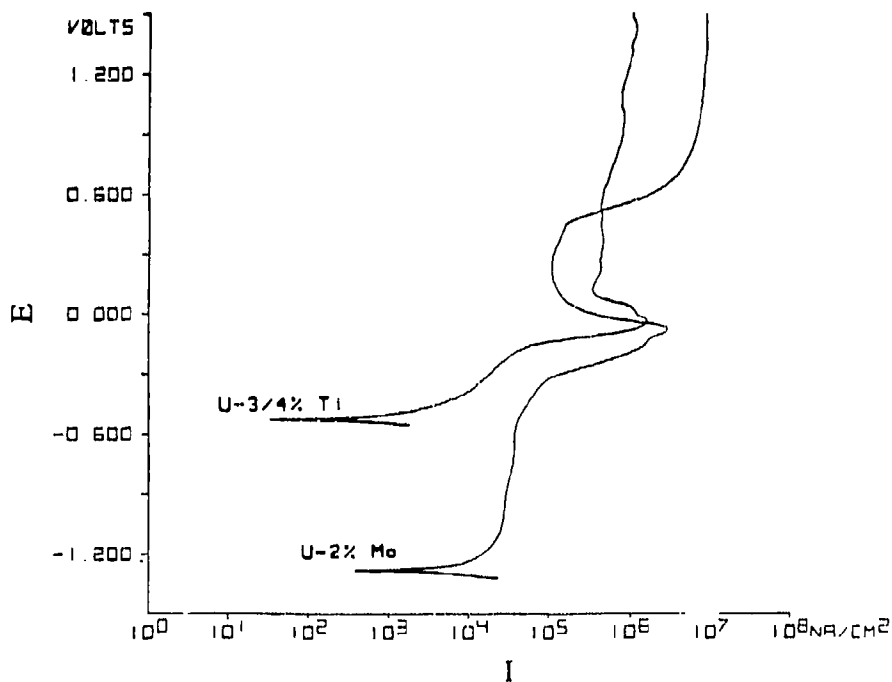


Figure 6. Potentiodynamic polarization curves for U-3/4% Ti and U-2% Mo in 1.0 M NaOH. Scan rate 1.388 mV/sec.

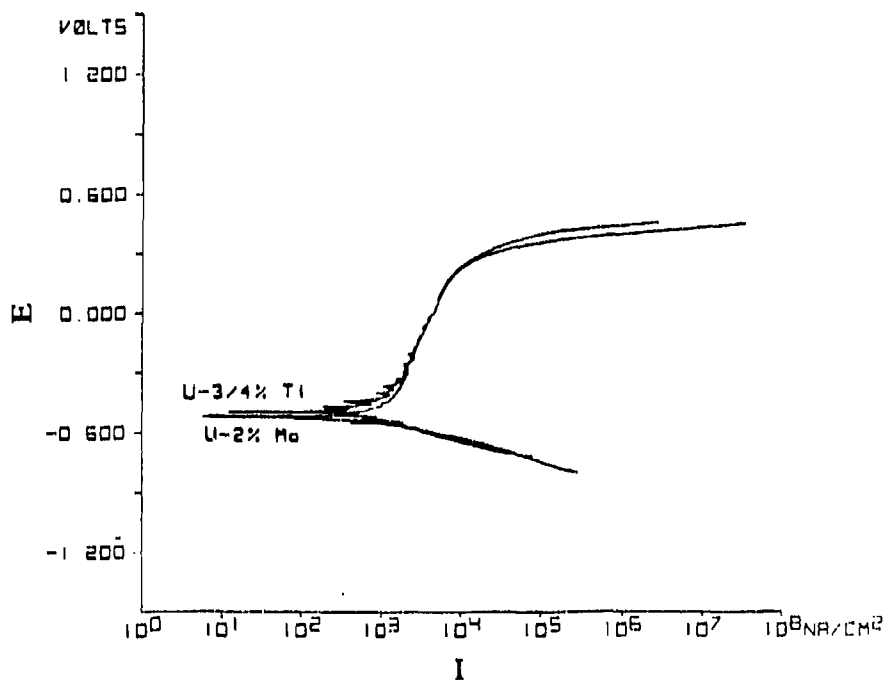


Figure 7. Potentiodynamic polarization curves for U-3/4% Ti and U-2% Mo in 1.0 N H₂SO₄. Scan rate 1.388 mV/sec.

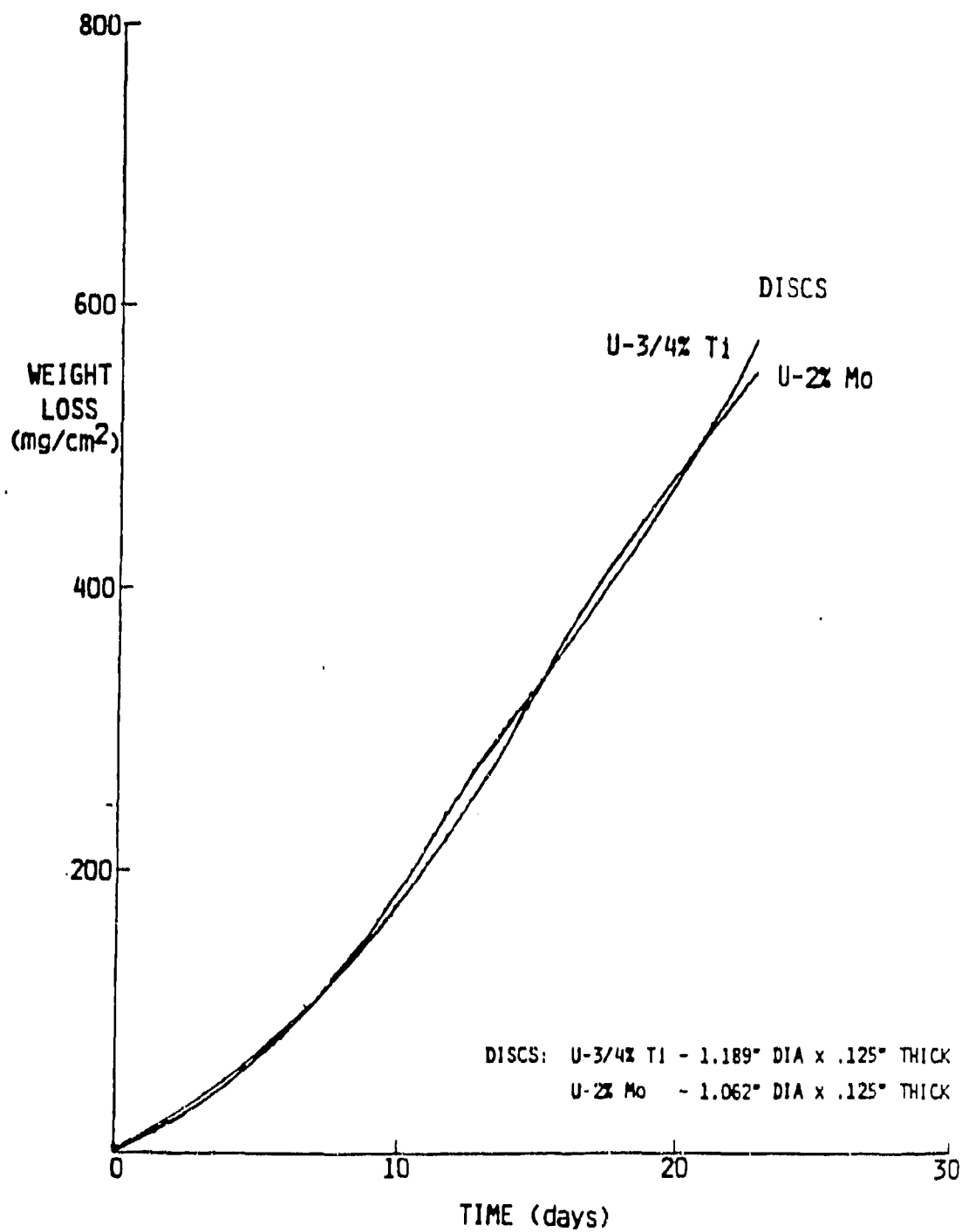


Figure 8. Weight loss of NMI M774 U-3/4% Ti and U.K. U-2% Mo discs in 5% salt fog environment at 35°C. (ASTM B 117-73)

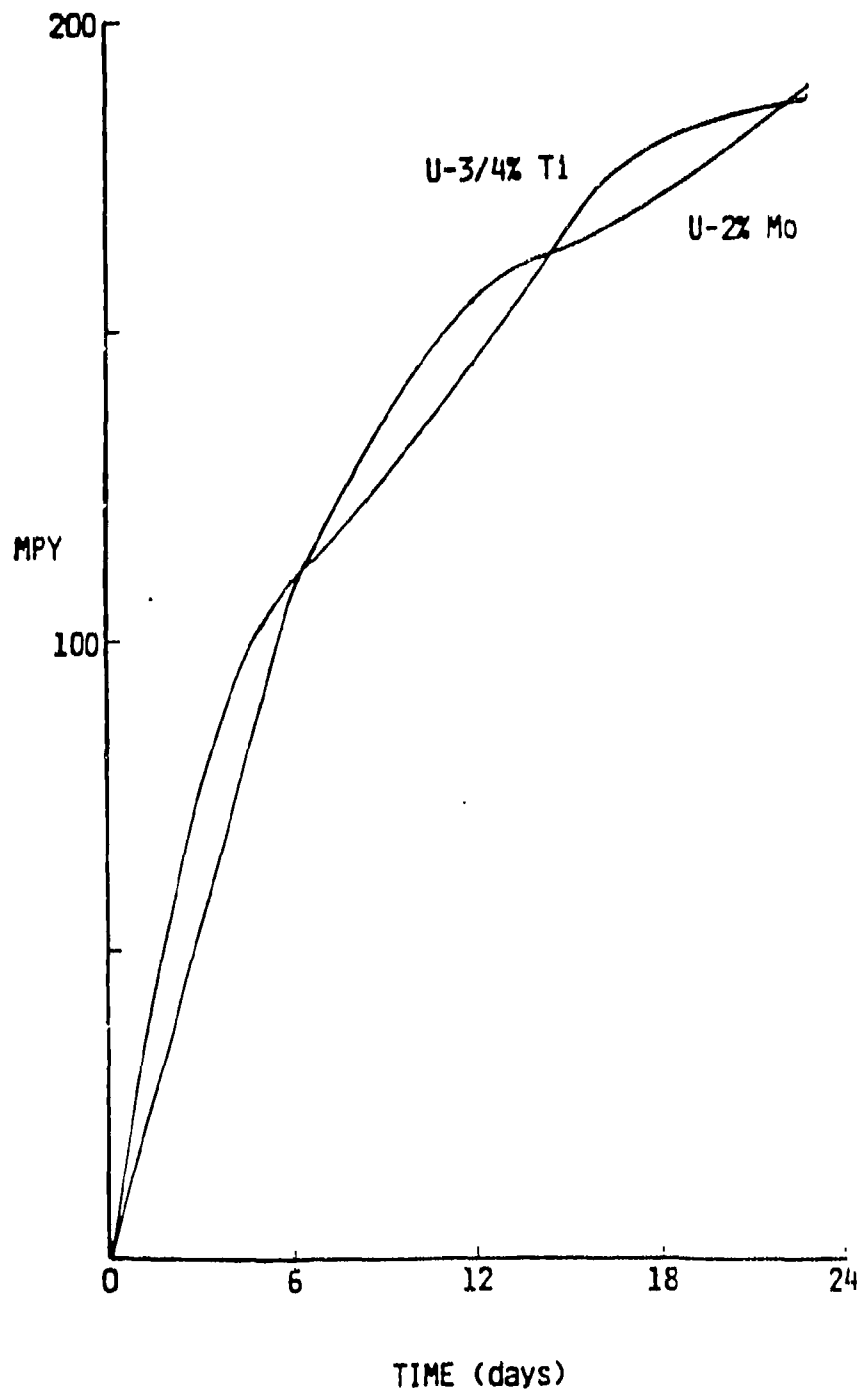
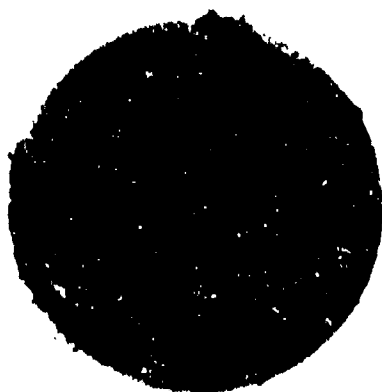
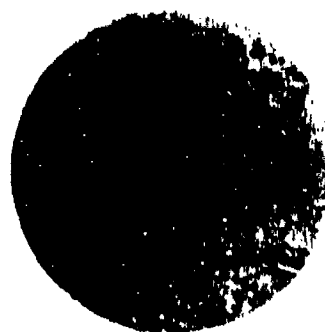


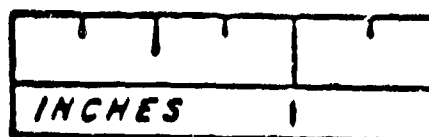
Figure 9. Corrosion rate of NMI M774 U-3/4% Ti and U.K. U-2% Mo discs in 5% salt fog environment at 35°C. (ASTM B 117-73)



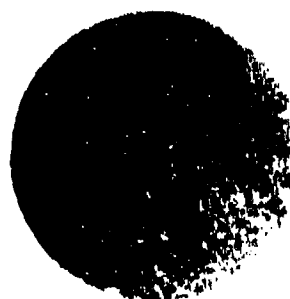
U-3/4% Ti



U-3/4% Ti

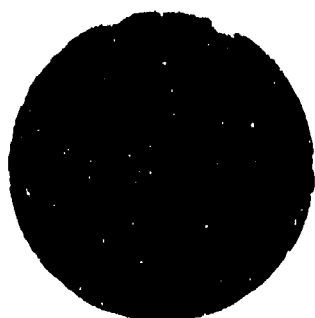


U-2% Mo
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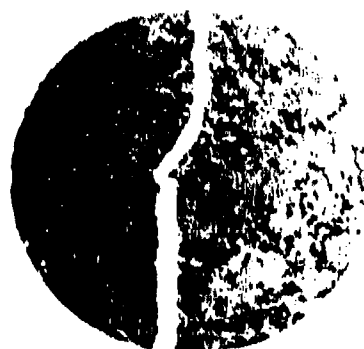
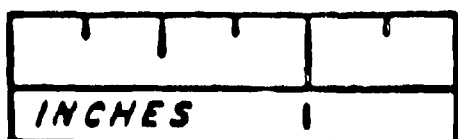


U-2% Mo
CLEANED

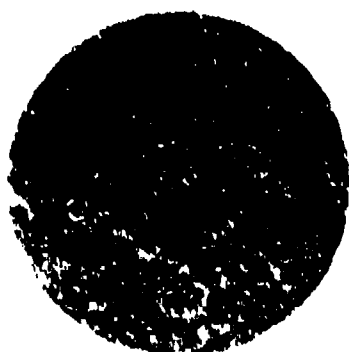
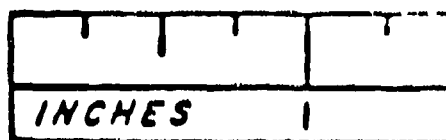
Figure 10. Specimens after a six day exposure in 5% salt fog.



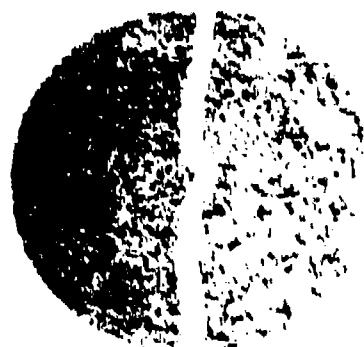
U-2% Mo



U-3/4% Ti

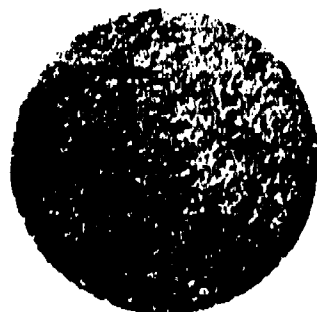


U-3/4% Ti

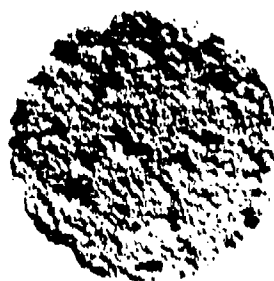
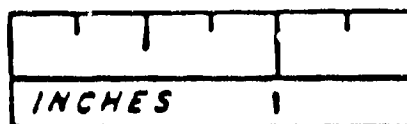


U-3/4% Ti

Figure 11. Specimens after a 12-day exposure in 5% salt fog cleaned with 20% HNO_3 .

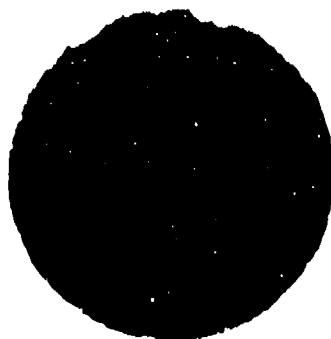


U-3/4% Ti

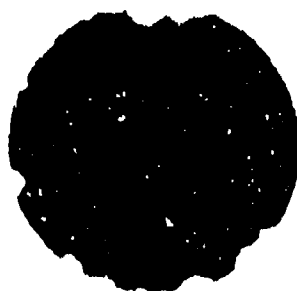
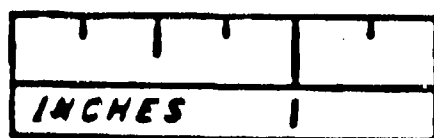


U-2% Mo

Figure 12. Specimens after a 16-day exposure
in 5% salt fog cleaned with 1% HNO₃.

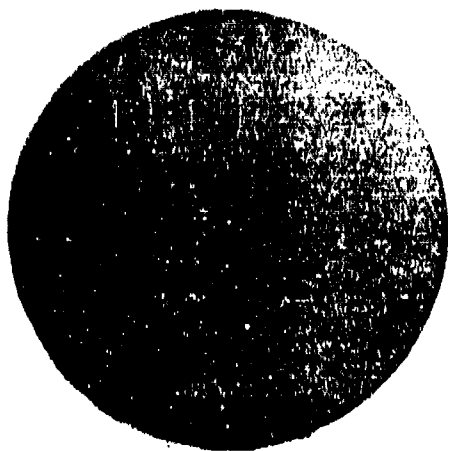


U-3/4% Ti

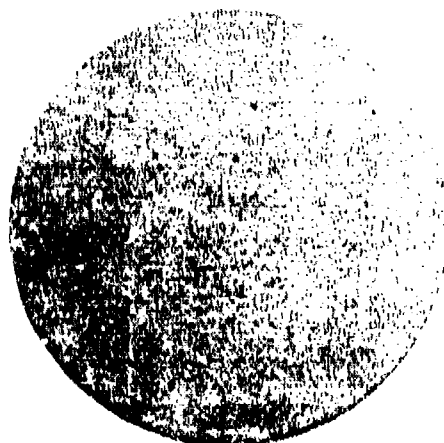


U-2% Mo

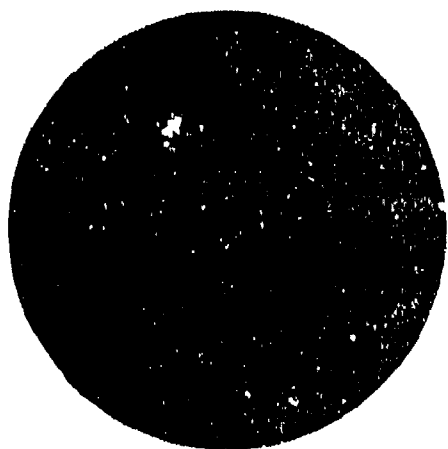
Figure 13. Specimens after a 23-day exposure
in 5% salt fog cleaned with 20% HNO₃.



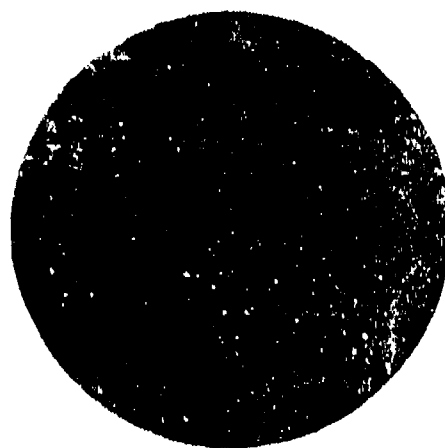
U-3/4% Ti
IVD Al-1.0 mil.



U-2% Mo
IVD Al-1.0 mil.

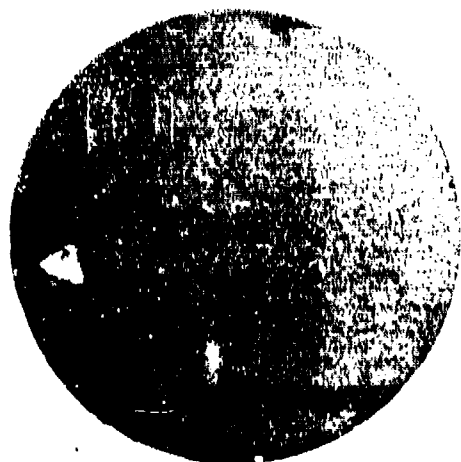


U-3/4% Ti
IVD Al-1.1 mil.

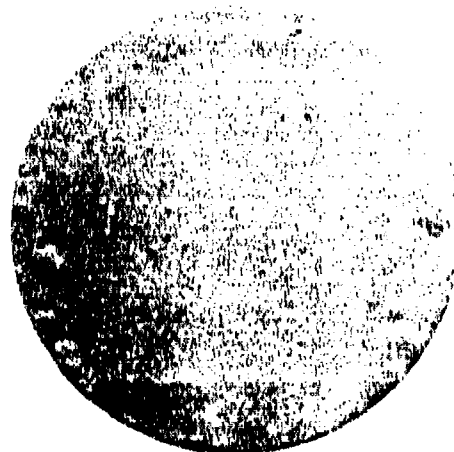


U-2% Mo
IVD Al-1.1 mil.

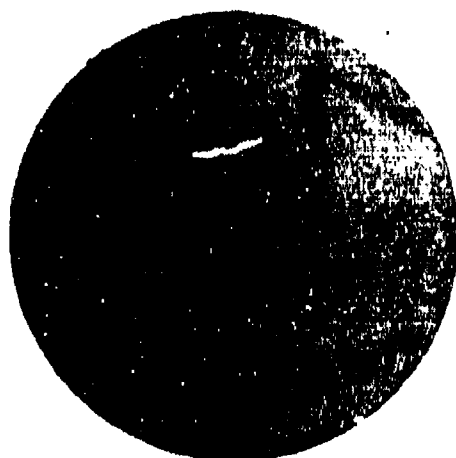
Figure 14. Specimens after a six day exposure in 5% salt fog.



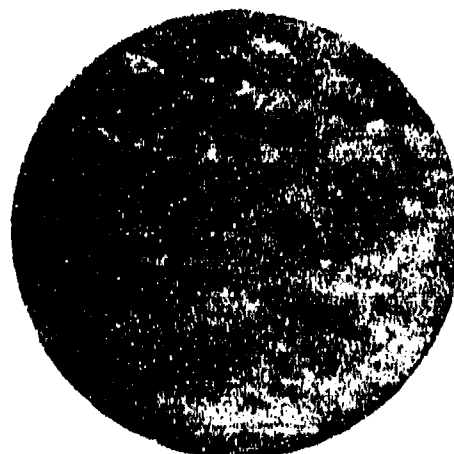
U-3/4% Ti
IVD Al-1.0 mil.



U-2% Mo
IVD Al-1.0 mil.



U-3/4% Ti
IVD Al-1.1 mil.

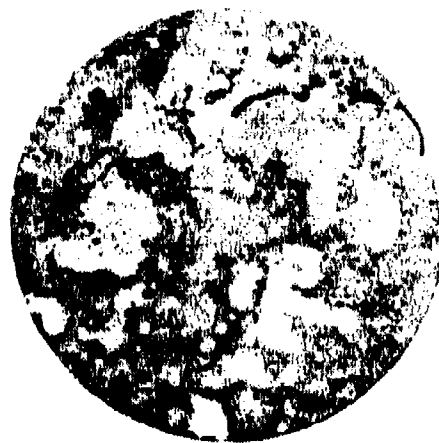


U-2% Mo
IVD Al-1.1 mil.

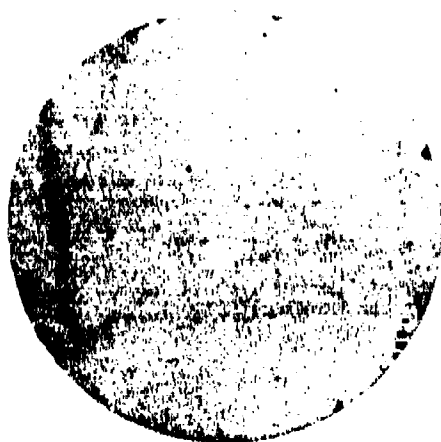
Figure 15. Specimens after a 12-day exposure in 5% salt fog.



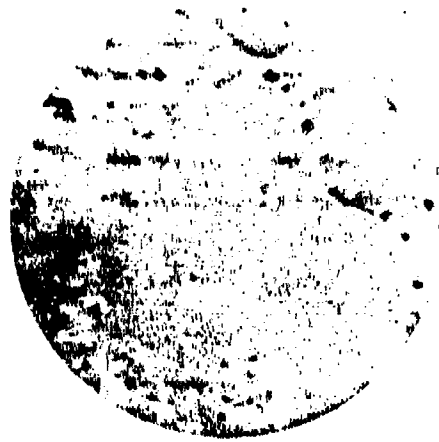
U-3/4% Ti
IVD Al-1.0 mil.



U-2% Mo
IVD Al-1.0 mil.



U-3/4% Ti
IVD Al-1.1 mil.

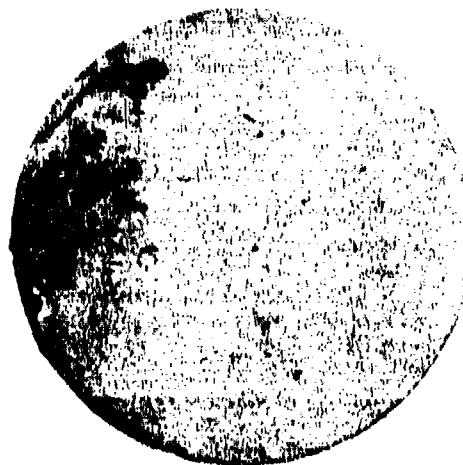


U-2% Mo
IVD Al-1.1 mil.

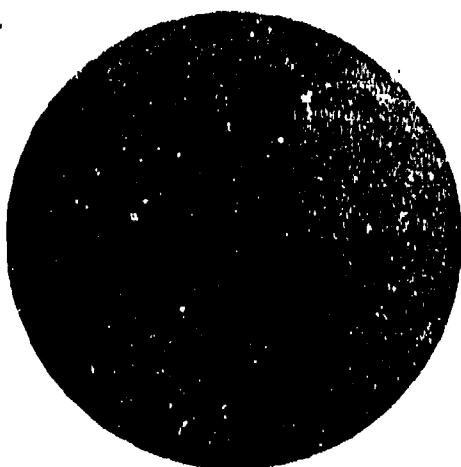
Figure 16. Specimens after a 19-day exposure in 5% salt fog.



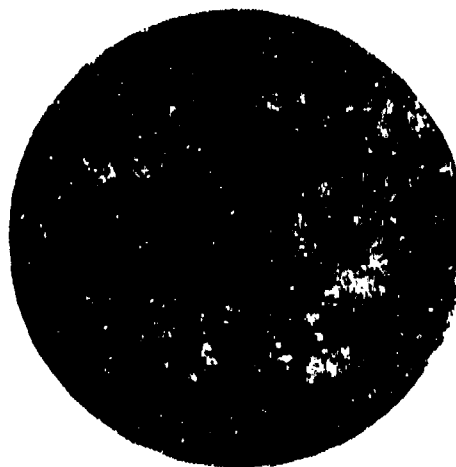
U-3/4% Ti
IVD Al-1.0 mil.



U-2% Mo
IVD Al-1.0 mil.



U-3/4% Ti
IVD Al-1.1 mil.



U-2% Mo
IVD Al-1.1 mil.

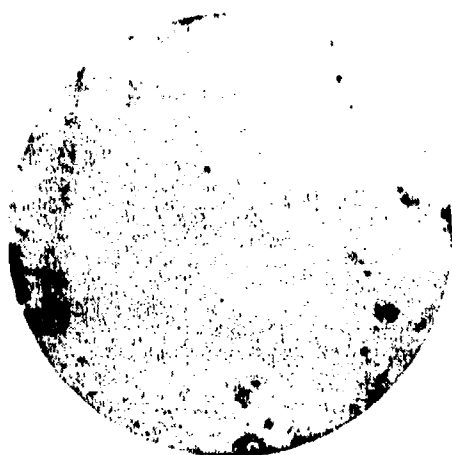
Figure 17. Specimens after a 23-day exposure in 5% salt fog.



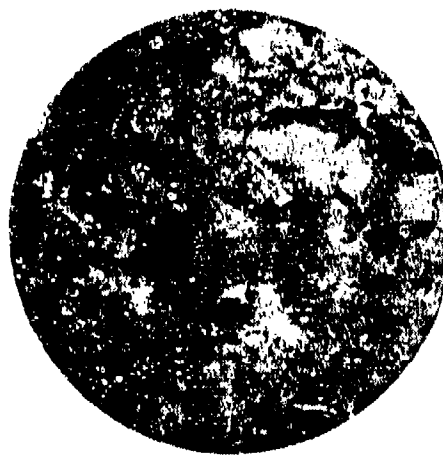
U-3/4% Ti
IVD Al-1.0 mil.



U-2% Mo
IVD Al-1.0 mil.



U-3/4% Ti
IVD Al-1.1 mil.



U-2% Mo
IVD Al-1.1 mil.

Figure 18. Specimens after a 28-day exposure in 5% salt fog.

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