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# MICROSTRUCTURAL EFFECTS ON THE STRESS CORROSION CRACKING BEHAVIOR OF Ti-8Al-1Mo-1V IN METHANOLIC AND CHLORIDE SOLUTIONS

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## ABSTRACT

The stress corrosion cracking behavior of Ti-8Al-1Mo-1V has been studied in several environments. Of the environments employed, methanol with a small addition of hydrochloric acid was found to be the most aggressive. Altering the microstructure of the alloy produced a marked improvement in resistance to stress corrosion cracking in distilled water and salt water media. The SCC susceptibility was also significantly decreased by the addition of sodium nitrate to both salt water and methanol plus hydrochloric acid environments. Fractographic analyses have been carried out and related to SCC behavior. (Authors)

## INTRODUCTION

Titanium, because of its attractive high strength-to-weight ratio and good general resistance to corrosion, continues to be a prime candidate material for many Army applications. Unfortunately, many of its alloys have been reported as susceptible to stress corrosion cracking (SCC) in a variety of environments such as salt water,<sup>1</sup> alcohols,<sup>2</sup> and methanol-hydrochloric acid solution.<sup>3,4</sup>

The stress corrosion behavior of titanium is significantly influenced by microstructure. Curtis and Spurr,<sup>5</sup> in their work with the alpha and beta titanium alloy 6Al-4V, found that solution treatment in the beta phase field resulted in the elimination of the large equiaxed alpha grains. This treatment rendered the alloy less susceptible to slow crack growth in salt water and improved both the fracture toughness and the threshold value for stress corrosion cracking. Curtis, Boyer, and Williams<sup>6</sup> later showed that beta-quenched alpha titanium alloy Ti-5Al-5Sn-5Zr was more susceptible to SCC than the alpha-quenched condition and attributed the difference in behavior to the martensite morphology.

The titanium alloy 8Al-1Mo-1V was chosen for our investigation because it was originally developed for moderately high temperature application in the compressor section of gas turbine engines. Furthermore, by selective heat treatments, significant increases in strength can be obtained<sup>7</sup> and different microstructures can be produced which, as reported by Curtis et al.<sup>5</sup> for other titanium alloys, can influence the SCC susceptibility of the alloy. Our study was aimed at improving the SCC behavior of annealed Ti-8Al-1Mo-1V by selective heat treatments which would provide a range of microstructures. As-received mill-annealed material was included for base-line data.

## EXPERIMENTAL PROCEDURE

### Materials

Mechanical property and SCC specimens were fabricated from 2-1/2-inch-square bar stock of titanium alloy 8Al-1Mo-1V having the following composition (in weight percent): 7.6 Al, 1.1 Mo, 1.1 V, 0.06 Fe, 0.005 H, 0.09 O, 0.022 C, 0.008 N, and balance Ti. In order to characterize the alloy's response to stress corrosion cracking for the two selected heat treat conditions, specimen blanks were heat

1. BROWN, B. F. *A New Stress Corrosion Cracking Test for High Strength Alloys*. Materials Research and Standards, v. 6, no. 3, March 1966, p. 129.
2. HANEY, E. G., and WEARMOUTH, W. R. *Effect of Pure Methanol on the Cracking of Titanium*. Corrosion, v. 25, 1969, p. 87.
3. MORI, K., TAKAMURA, A., and SHIMOSE, T. *Stress-Corrosion Cracking of Titanium and Zirconium in HCl-Methanol Solutions*. Corrosion, v. 22, 1966, p. 29.
4. LEVY, M., and SEITZ, D. *Stress Corrosion Cracking of Ti-8Al-1Mo-1V Alloy in Methanol-Hydrochloric Acid Solutions*. Corrosion Science, May 1969, p. 341-351; also Army Materials and Mechanics Research Center, AMMRC TR 68-21, November 1968.
5. CURTIS, R. E., and SPURR, S. F. *Effect of Microstructure on the Fracture Properties of Titanium Alloys in Air and Salt Solution*. ASM Transactions Quarterly, v. 61, 1968, p. 115.
6. CURTIS, R. E., BOYER, R. R., and WILLIAMS, J. C. *Relationship Between Composition, Microstructure, and Stress Corrosion Cracking (in Salt Solution) in Titanium Alloys*. ASM Transaction Quarterly, v. 62, 1969, p. 457.
7. FOPIANO, P. J., and HICKEY, C. F., Jr. *The Effect of Heat Treatment on the Mechanical Properties of the Alloy Ti-8Al-1Mo-1V*. Army Materials and Mechanics Research Center, AMMRC TR 73-17, April 1973.

treated prior to final machining and fatigue precracking. In all cases, including the mill-annealed condition, the specimens were cut with the long dimension parallel to the rolling direction and notched to cause crack growth to take place through the original bar thickness (L-T orientation).

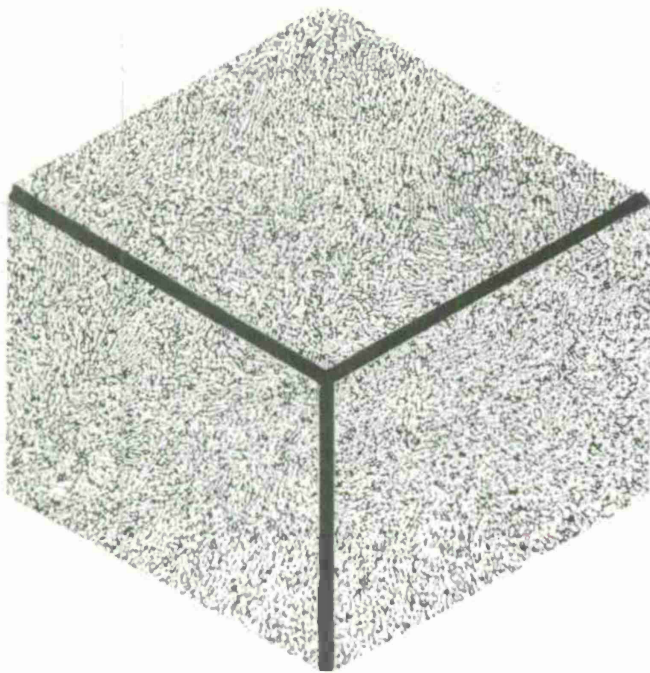
The mechanical properties of the alloy together with the specific heat treatments for each condition are shown in Table 1. It should be noted that the ultimate tensile strength and 0.2% offset yield strength were essentially the same for the two selected heat treatments. However, the reductions in area were significantly different, which indicates that solution treating at 1825 F in the alpha-beta field and subsequent aging results in a more ductile alloy condition than solution treating at 1950 F above the beta transus. The mill-annealed alloy had the lowest strength and the highest ductility.

Table 1. MECHANICAL PROPERTIES AND HEAT TREATMENT OF Ti-8Al-1Mo-1V ALLOY

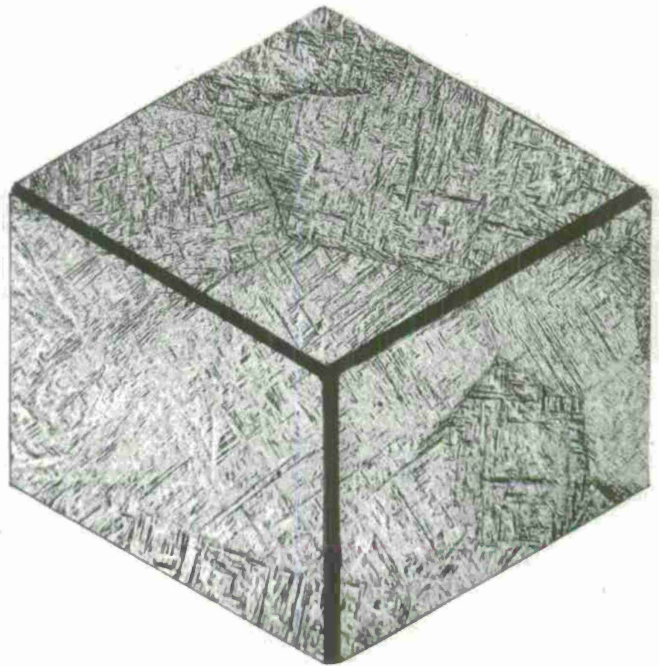
Condition	0.2% Y.S. (ksi)	U.T.S. (ksi)	Elong. (%)	R.A. (%)
Mill-Annealed 70% Forged 1850 F Annealed 1450 F/1 hr/FC	120.3	133.4	20.3	39.8
Beta-Treated 1950 F/1 hr/WQ Aged 900 F/1 hr/AC	138.5	158.5	8.0	15.2
Alpha + Beta-Treated 1825 F/1 hr/WQ Aged 900 F/1 hr/AC	138.7	156.9	12.9	39.2

Microstructures for the mill-annealed and the two heat treat conditions are shown in Figure 1. The as-received mill-annealed material (Figure 1a) has a fine-grained equiaxed alpha and intergranular beta structure. The fine grains are due to working (70% forged at 1850 F) in the alpha-beta field. The alloy which was solution treated above the beta transus (~1930 F) has an alpha prime or titanium martensite structure as shown in Figure 1b, while solution treating the alloy at 1825 F and aging resulted in a mixed microstructure composed of almost equal amounts of an equiaxed alpha phase (white) and a transformed beta grayish phase. The grayish transformed beta phase is a mixture of alpha and beta with the alpha phase probably precipitating in the beta during aging. Volume fraction of the phases was determined by lineal analysis and was found to be approximately 60 percent alpha and 40 percent beta for the latter condition. The volume fraction for the mill-annealed material was 90 percent alpha and 10 percent beta.

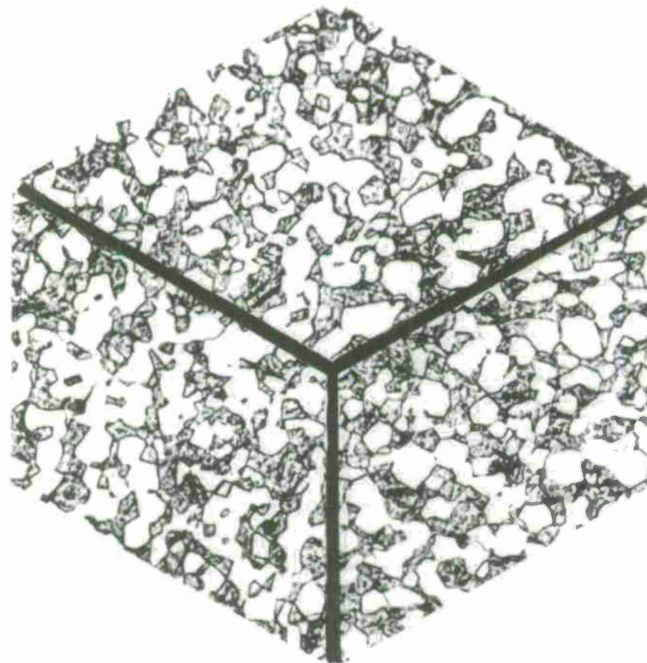
The environments used for testing were distilled water, 3.5% aqueous sodium chloride solution, methyl alcohol, and methyl alcohol to which a small amount of hydrochloric acid (0.4%) was added. Distilled water was included because some titanium alloys in certain heat treatment conditions are susceptible to SCC in distilled water. Also, the information generated in distilled water gives a basis for comparing the effects of specificity of ions (such as Cl<sup>-</sup>) in solution. Reagent grade chemicals and distilled water were used to prepare the test solutions.



a. As-received, 70% forged 1850 F,  
annealed 1450 F/8 hr/FC, Mag. 75X



b. Beta-treated, 1950 F/1 hr/WQ,  
aged 900 F/1 hr/AC, Mag. 37.5X



c. Alpha + beta-treated, 1825 F/1 hr/WQ,  
aged 900 F/1 hr/AC, Mag. 375X

Figure 1. Microstructures of Ti-8Al-1Mo-1V alloy.

## Specimens and Test Procedure

The cantilever beam stress corrosion cracking test was used to determine the effect of heat treatment on the SCC resistance of the alloy. The test procedure has been described in detail elsewhere.<sup>8</sup> The test apparatus and the geometry and size of specimens are shown in Figure 2 along with the Kies equation which is used to reduce the data to stress intensity. To evaluate the alloy, the specimen is first stressed in air at increasing loads until it fractures. The data are reduced to stress intensity using the Kies equation. Having established the stress intensity for "dry" conditions,  $K_{IX}$ , a specimen is similarly tested in the desired solution at a somewhat lower stress intensity. If the specimen did not fail within 6 hours, the stress intensity was increased by ~3% each succeeding 6 hours until failure occurred and the time required for rupture noted.  $K_{ISCC}$  was determined from a plot of stress intensity versus time-to-failure and is defined as the stress intensity below which SCC will not occur.

Fractured surfaces were replicated by the two-stage plastic carbon technique and examined by electron microscopy. Chromium was used as a pre-shadowing material.

## RESULTS AND DISCUSSION

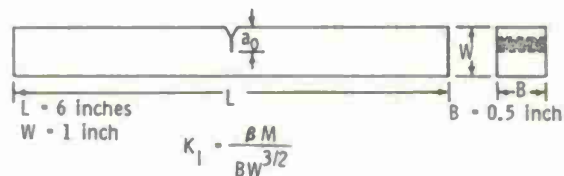
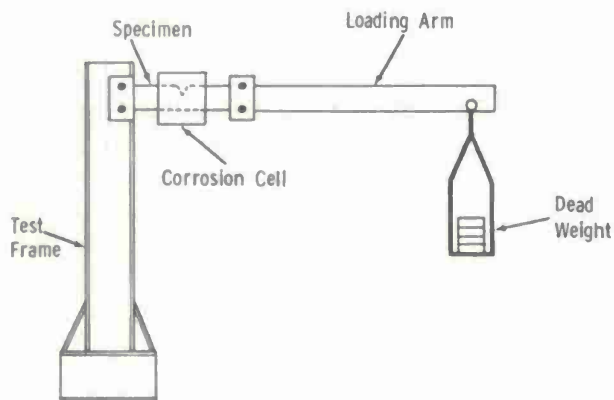
### $K_{ISCC}$ Determination

The  $K_{ISCC}$  for the alloy in the three different heat-treated conditions was determined for each environment from a plot of stress intensity versus time to failure. The results are shown in bar graph form in Figure 3. For simplicity, the mill-annealed structure will be henceforth referred to as A; the structure resulting from treating in the beta phase field (1950 F) as B; and the structure resulting from treating in the alpha + beta field (1825 F) as C. Figure 3 shows that  $K_{ISCC}$  in distilled water is 65  $\text{ksi}\sqrt{\text{in.}}$  for structure B; 58  $\text{ksi}\sqrt{\text{in.}}$  for structure C; and 44  $\text{ksi}\sqrt{\text{in.}}$  for structure A. The air values for those structures are 73  $\text{ksi}\sqrt{\text{in.}}$ , 58  $\text{ksi}\sqrt{\text{in.}}$ , and 61  $\text{ksi}\sqrt{\text{in.}}$ . Thus, the alloy in condition C is immune to SCC in distilled water, ( $K_{ISCC}/K_{IX}$ ) = 1.0, while structure B is essentially immune ( $K_{ISCC}/K_{IX}$ ) = 0.89, and structure A shows some susceptibility ( $K_{ISCC}/K_{IX}$ ) = 0.72. The values obtained for the 3.5% sodium chloride environment show that structure C, again, is essentially immune to SCC and that structure A is, again, more susceptible to SCC than structure B. Also shown in Figure 3 is the beneficial effect of  $\text{NaNO}_3$  in mitigating SCC in the 3.5% sodium chloride solution. Note that  $K_{ISCC}$  in distilled water and inhibited salt solution is identical for structure B and within experimental error for structure A, which demonstrates the efficacy of  $\text{NaNO}_3$  in combatting the aggressiveness of the chloride ion. Since structure C was essentially immune to SCC in NaCl environment, it was not tested in the inhibited NaCl solution.

The data obtained for the alloy in the three different heat treatment conditions in methanolic solutions indicate that these structures exhibit a high and similar degree of susceptibility to SCC, with the  $\text{CH}_3\text{OH} + 0.4\% \text{HCl}$  medium being

8. CZYRKLIS, W. F., and LEVY, M. *Stress Corrosion Cracking Behavior of Uranium Alloys*. Corrosion, v. 30, no. 5, May 1974, p. 181-187; also Army Materials and Mechanics Research Center, AMMRC TR 73-54, December 1973.





where:

M = the bending moment at the notch

B = the thickness of the specimen

W = the depth of the specimen

$$\beta = 4.12 \sqrt{\frac{1}{(1-a/W)^3} - (1-a/W)^3}$$

Figure 2. Cantilever test rig and equation for determining  $K_{I,SCC}$ .

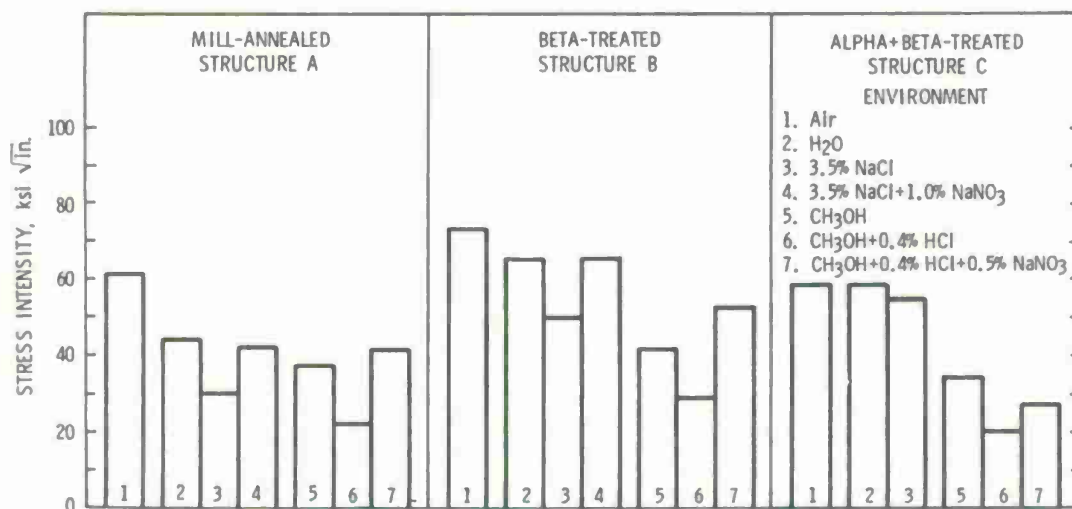


Figure 3. Comparison of SCC susceptibility of Ti-8Al-1Mo-1V.

the most aggressive environment. Structure A showed a greater susceptibility to SCC in the NaCl environment than in CH<sub>3</sub>OH, whereas structures B and C were more susceptible in CH<sub>3</sub>OH. When specimens were stress corroded in CH<sub>3</sub>OH + 0.4% HCl to which NaNO<sub>3</sub> was added, structure A showed the same marked improvement as in the inhibited NaCl solution, structure B showed somewhat less but still significant improvement, and structure C was relatively unaffected by NaNO<sub>3</sub>.

A summary of the SCC results obtained along with the "susceptibility ratio"  $K_{I,SCC}/K_{I,X}$  are shown in Table 2.

### Fractography

Figures 4 to 10 present high magnification replica fractographs for each alloy heat treatment condition showing the effect of environment on the fracture mode. The predominant mode of failure in air for the alloy in the three conditions (Figure 4) under fast fracture is transgranular dimpled rupture. Both alpha and beta phases are clearly delineated in condition C. In distilled water, Figure 5, the fracture mode in the slow crack growth (SCC) region for conditions A

Table 2. SUMMARY OF Ti-8Al-1Mo-1V SCC RESULTS

Environment	Structure					
	A		B		C	
	Mill-Annealed		Beta-Treated		Alpha + Beta-Treated	
	133.4 ksi U.T.S. 120.3 ksi Y.S.		158.5 ksi U.T.S. 138.5 ksi Y.S.		156.9 ksi U.T.S. 138.7 ksi Y.S.	
	$\frac{K}{\text{ksi}\sqrt{\text{in.}}}$	$\frac{K_{ISCC}}{K_{IX}}$	$\frac{K}{\text{ksi}\sqrt{\text{in.}}}$	$\frac{K_{ISCC}}{K_{IX}}$	$\frac{K}{\text{ksi}\sqrt{\text{in.}}}$	$\frac{K_{ISCC}}{K_{IX}}$
Air	61	-	73	-	58	-
Water	44	0.72	65	0.89	58	1.0
3.5% NaCl	30	.49	50	.68	54	0.93
3.5% NaCl + 1.0% NaNO <sub>3</sub>	42	.69	65	.89	-	-
CH <sub>3</sub> OH	37	.61	41	.56	34	.59
CH <sub>3</sub> OH + 0.4% HCl	22	.36	29	.40	20	.34
CH <sub>3</sub> OH + 0.4% HCl + 0.5% NaNO <sub>3</sub>	41	.67	52	.71	27	.47

and B is cleavage while condition C, which exhibited immunity to SCC in water, has the same fracture mode that was observed for failure in air, namely, ductile rupture of the alpha phase and tearing of the beta phase. The predominant mode of fracture in 3.5% NaCl environment (Figure 6) was quasi cleavage for all three conditions. Note the similarity in fracture topography for condition B in water and in NaCl. Figure 7 shows that structure A failed by a cleavage mode when exposed to 3.5% NaCl solution to which NaNO<sub>3</sub> was added, which was also the case upon exposure to distilled water. Figure 7 also shows that condition B failed by ductile rupture rather than cleavage which is reflected in the higher threshold for SCC.

Specimens which failed in methanolic environments, Figures 8 to 10, exhibit transgranular cleavage for all heat treatment conditions. However, there is evidence of ductile fracture of the beta or martensitically transformed beta regions as shown for conditions B and C. For condition A the cleavage mode of river patterns and cleavage steps changes to one of small faceted quasi cleavage when NaNO<sub>3</sub> is added to the methanolic solutions. A summary of the influence of environment and microstructure on the fracture behavior of Ti-8Al-1Mo-1V is contained in Table 3.

## CONCLUSIONS

1. The SCC resistance of Ti-8Al-1Mo-1V in aqueous solutions based on the relative susceptibility ratio  $K_{ISCC}/K_{IX}$  increases in the order: mill anneal, beta STA, and alpha + beta STA. Thus, solution treatment temperatures which increased the amount of martensite increased the SCC resistance of the alloy.

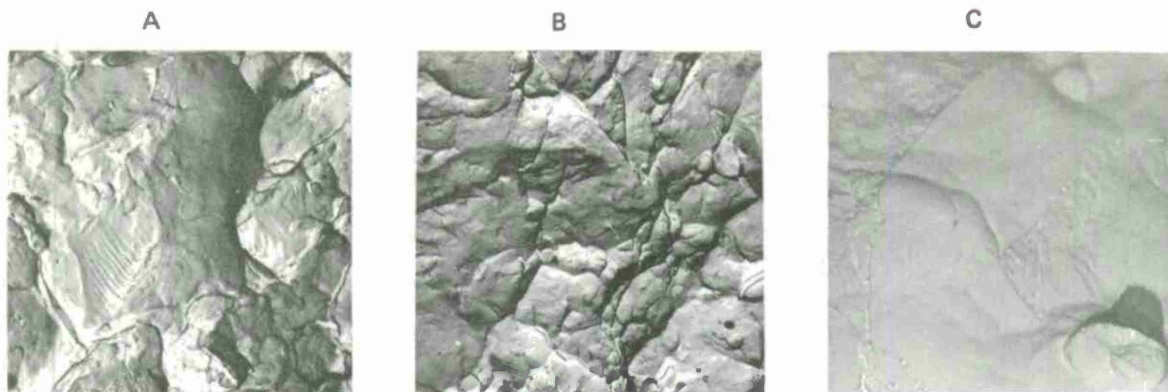


Figure 4. Air, Mag. (A) 1710X; (B) 2940X; (C) 3000X.



Figure 5. Water, Mag. (A) 4320X; (B) 1680X; (C) 1800X.



Figure 6. 3.5% NaCl, Mag. (A) 1500X; (B) 1800X; (C) 2130X.

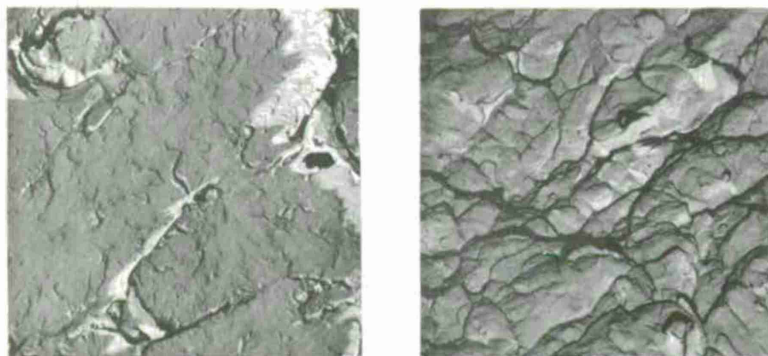


Figure 7. 3.5% NaCl + 1.0% NaNO<sub>3</sub>.  
(Structure C not tested.)  
Mag. (A) 3960X; (B) 2950X.

Figures 4 to 7. Fractographs of Ti-8Al-1Mo-1V resulting from failures in varied environments.

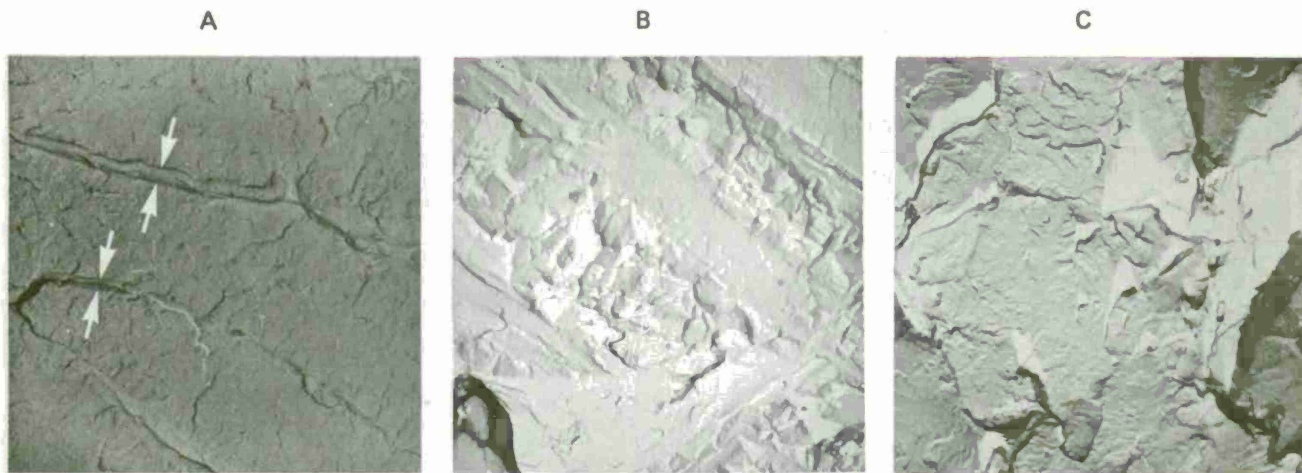


Figure 8.  $\text{CH}_3\text{OH}$ , Mag. (A) 4235X; (B) 2170X; (C) 3010X. (Arrows indicate cleavage steps.)

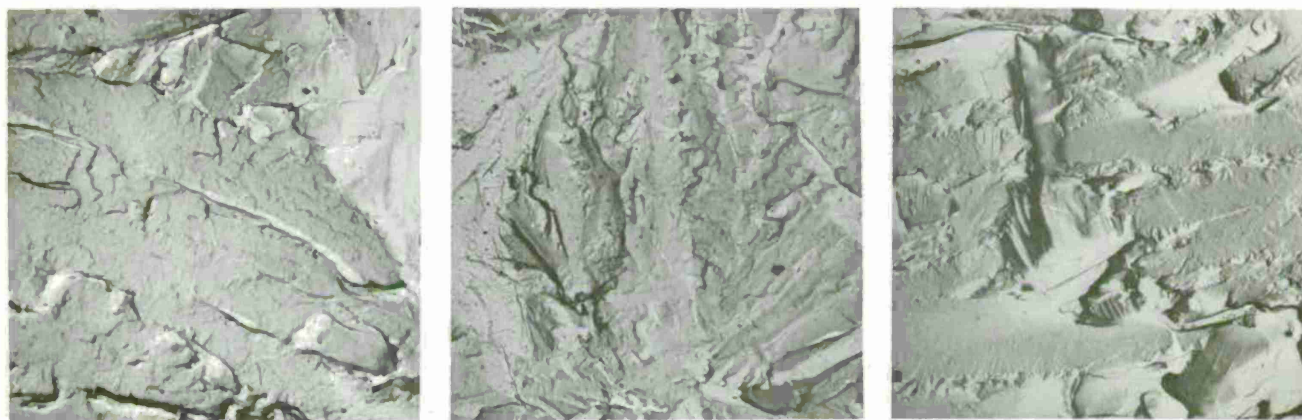


Figure 9.  $\text{CH}_3\text{OH} + 0.4\% \text{HCl}$ , Mag. (A) 1610X; (B) 1995X; (C) 1890X.

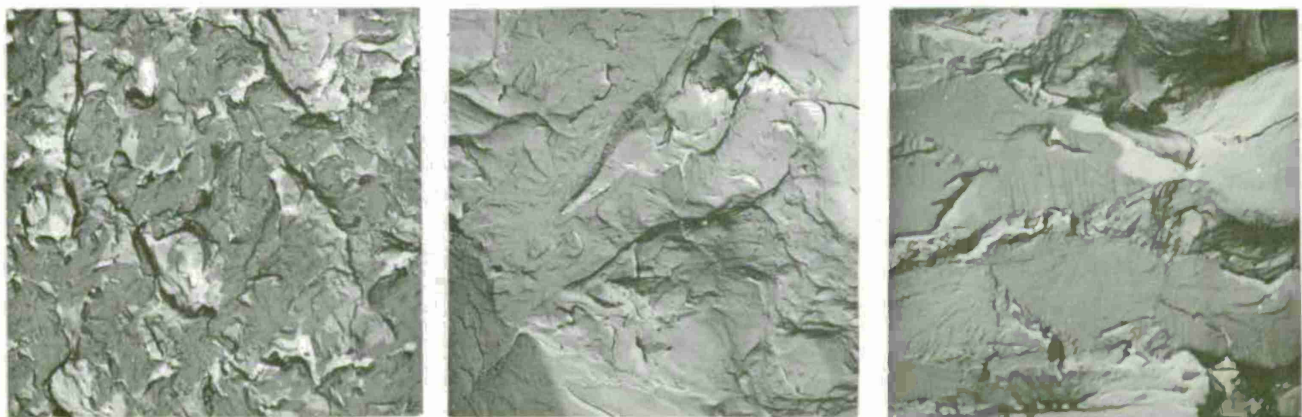


Figure 10.  $\text{CH}_3\text{OH} + 0.4\% \text{HCl} + 0.5\% \text{NaNO}_3$ , Mag. (A) 4410X; (B) 3990X; (C) 3430X.

Figures 8 to 10. Fractographs of Ti-8Al-1Mo-1V resulting from failures in methanolic environments.

Table 3. SUMMARY OF THE INFLUENCE OF ENVIRONMENT ON THE FRACTURE BEHAVIOR OF Ti-8Al-1Mo-1V

Environment	Structure		
	A Mill-Annealed	B Beta-Treated	C Alpha + Beta-Treated
Air	Plastic fracture, normal mode (ductile dimple), also ripples	Normal plastic fracture large and small dimples	Ductile rupture of alpha phase; "tearing" of beta phase
Water	Cleavage	Quasi cleavage	Ductile rupture as in air, both phases well defined
3.5% NaCl	Quasi cleavage	Quasi cleavage similar to water environment	Cleavage of alpha, ductile rupture of beta
3.5% NaCl + 1.0% NaNO <sub>3</sub>	Cleavage	Dimple rupture	Not tested
CH <sub>3</sub> OH	Cleavage	Cleavage plus ductile dimples	Quasi cleavage, relatively large facets
CH <sub>3</sub> OH + 0.4% HCl	Cleavage	Cleavage plus ductile	Cleavage of alpha, ductile rupture of beta
CH <sub>3</sub> OH + 0.4% HCl + 0.5% NaNO <sub>3</sub>	Quasi cleavage, relatively small facets	Quasi cleavage	Cleavage of alpha, ductile rupture of beta

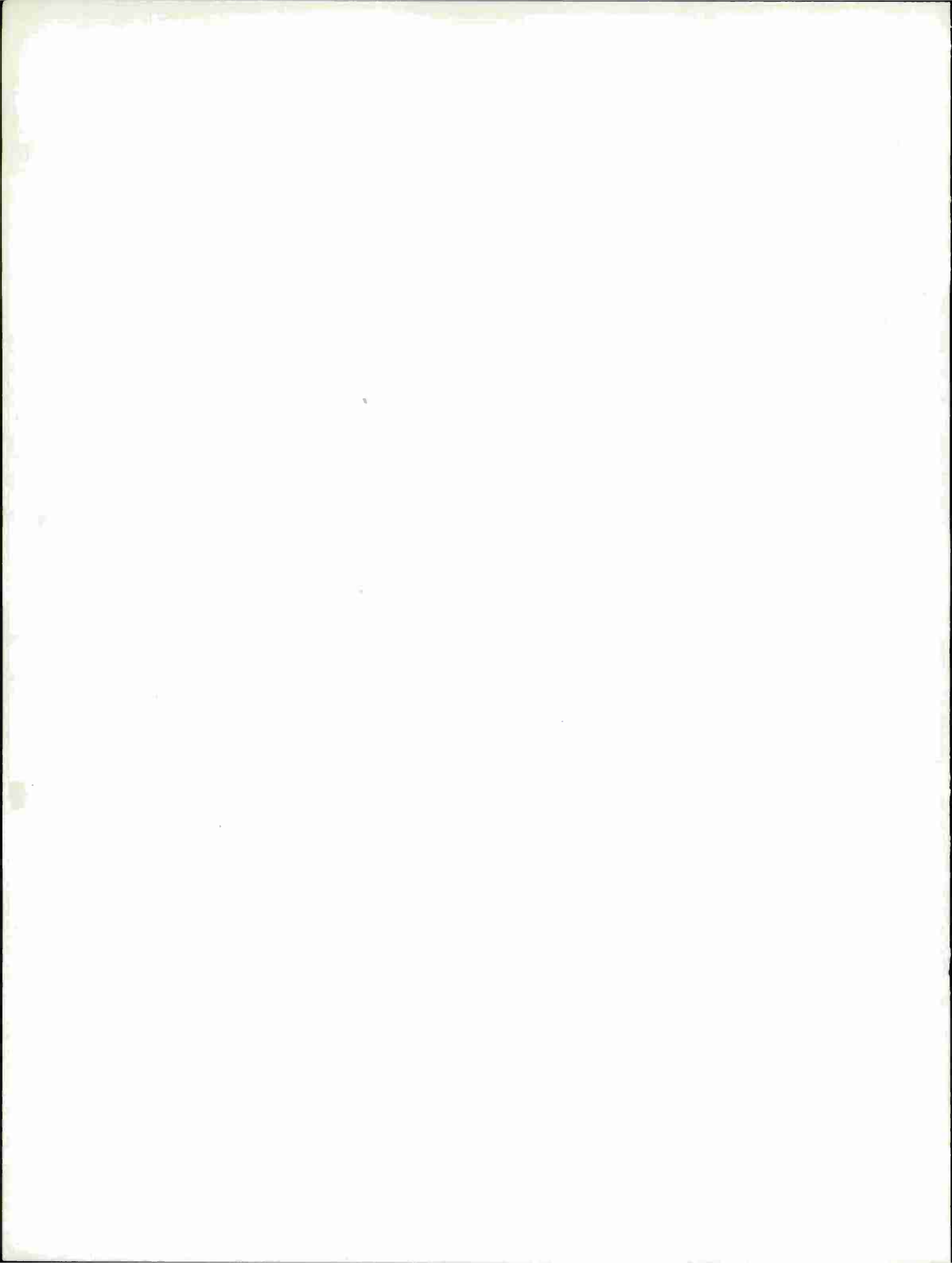
The alloy was more susceptible to SCC in methanolic solutions than in aqueous media regardless of heat treatment and susceptibility ratios were comparable for all three heat treatments. However, based on  $K_{ISCC}$  values only, the beta STA material appears to be the most SCC resistant in all environments.

2. The effectiveness of NaNO<sub>3</sub> as a SCC inhibitor for Ti-8Al-1Mo-1V is dependent on the heat treatment and the environment (aqueous or methanolic). In aqueous solutions, NaNO<sub>3</sub> added to 3.5% NaCl raises  $K_{ISCC}$  to the distilled water level. In methanol and hydrochloric acid, NaNO<sub>3</sub> is very effective when the alloy is in the beta STA condition, but is much less effective for the alpha + beta STA heat-treated alloy.

3. Fractographic analysis of the stress-corroded specimens showed that crack extension in the alloy for all heat treatments studied and in all environments was transgranular. The predominant mode of failure in aqueous and methanolic solutions was brittle, cleavage-like fracture. The alloy in all heat treat conditions exhibited fractographic ductile characteristics in air and in inhibited NaCl solution. In the beta STA condition the alloy also failed in a ductile manner in distilled water. Beta and martensitically transformed beta regions exhibited ductile characteristics while the alpha phase failed by a brittle cleavage mode. Because of this difference in phases, the heat treatments employed that changed the amount and morphology of the alpha + beta phases also influenced the susceptibility of the alloys to SCC.

#### ACKNOWLEDGMENT

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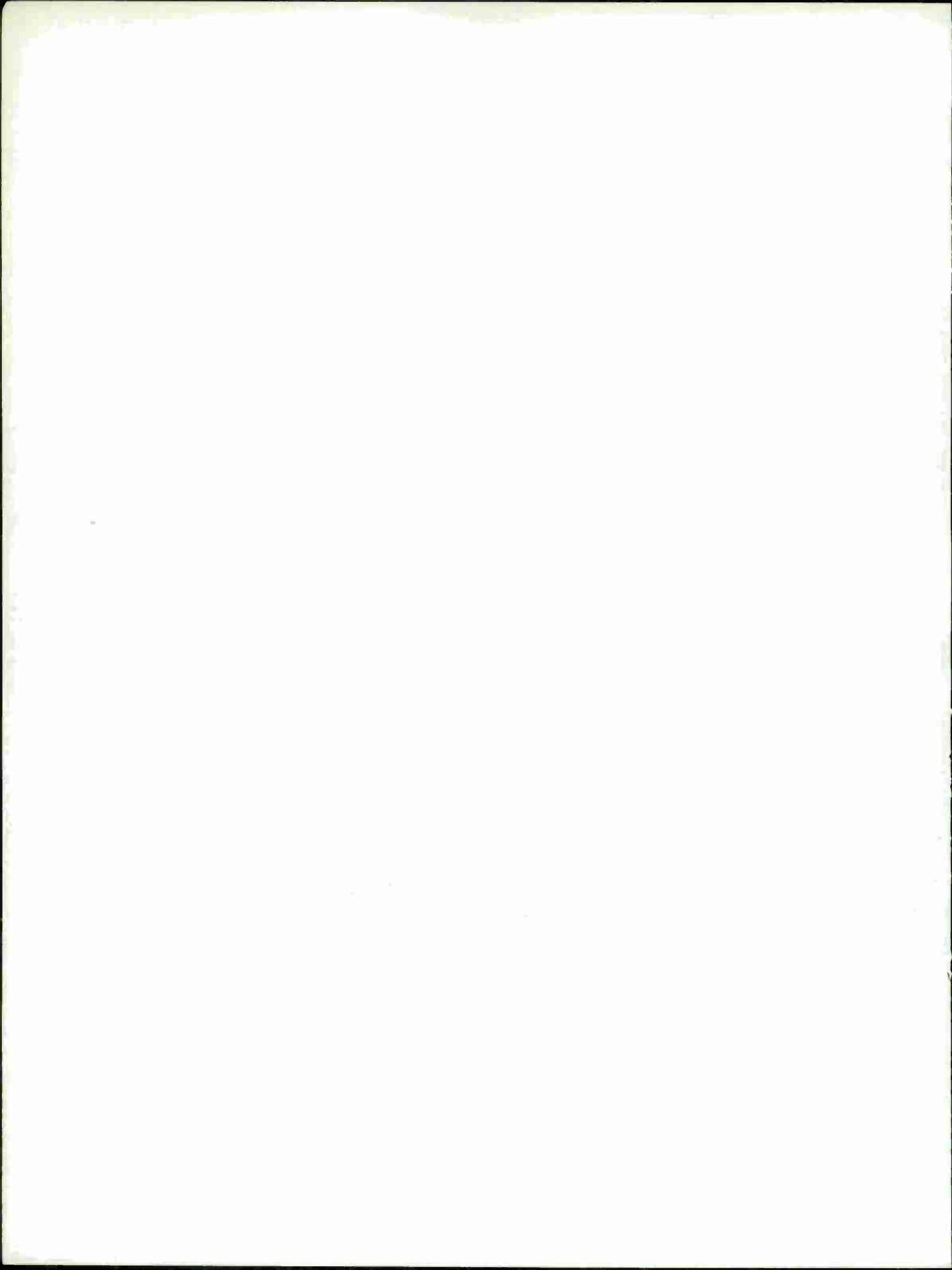
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Army Materials and Mechanics Research Center,  
Watertown, Massachusetts 02172  
MICROSTRUCTURAL EFFECTS ON THE STRESS CORROSION  
CRACKING BEHAVIOR OF Ti-8Al-1Mo-1V IN  
METHANOLIC AND CHLORIDE SOLUTIONS -  
Walter F. Czyrkliis and Milton Levy

Technical Report AMMRC TR 75-21, October 1975, 11 pp -  
illus-tables, D/A Project 1T162105AH84,  
AMCMS Code 612105.11.H8400

The stress corrosion cracking behavior of Ti-8Al-1Mo-1V has been studied in several environments. Of the environments employed, methanol with a small addition of hydrochloric acid was found to be the most aggressive. Altering the microstructure of the alloy produced a marked improvement in resistance to stress corrosion cracking in distilled water and salt water media. The SCC susceptibility was also significantly decreased by the addition of sodium nitrate to both salt water and methanol plus hydrochloric acid environments. Fractographic analyses have been carried out and related to SCC behavior.

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Key Words  
Microstructure  
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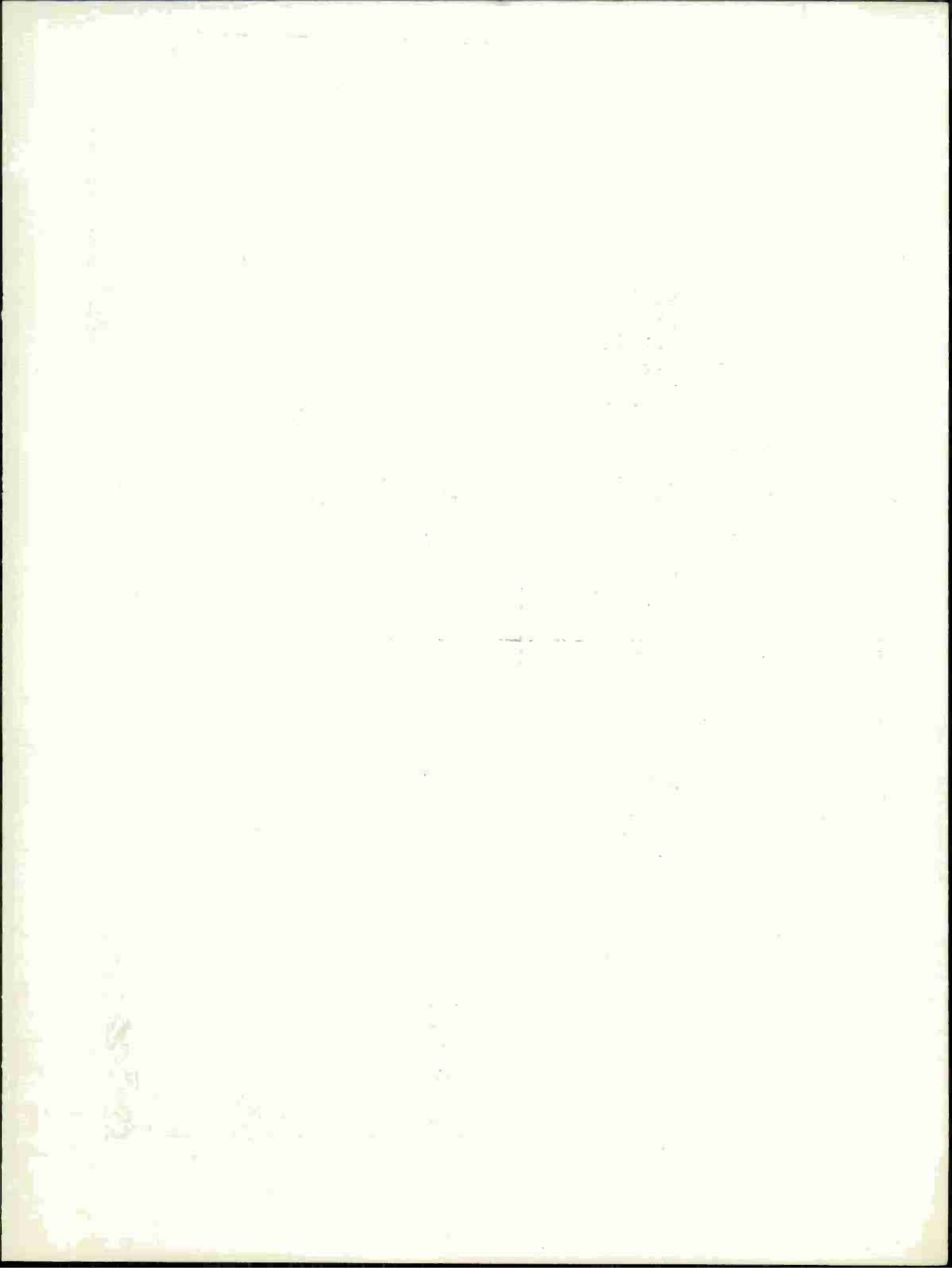
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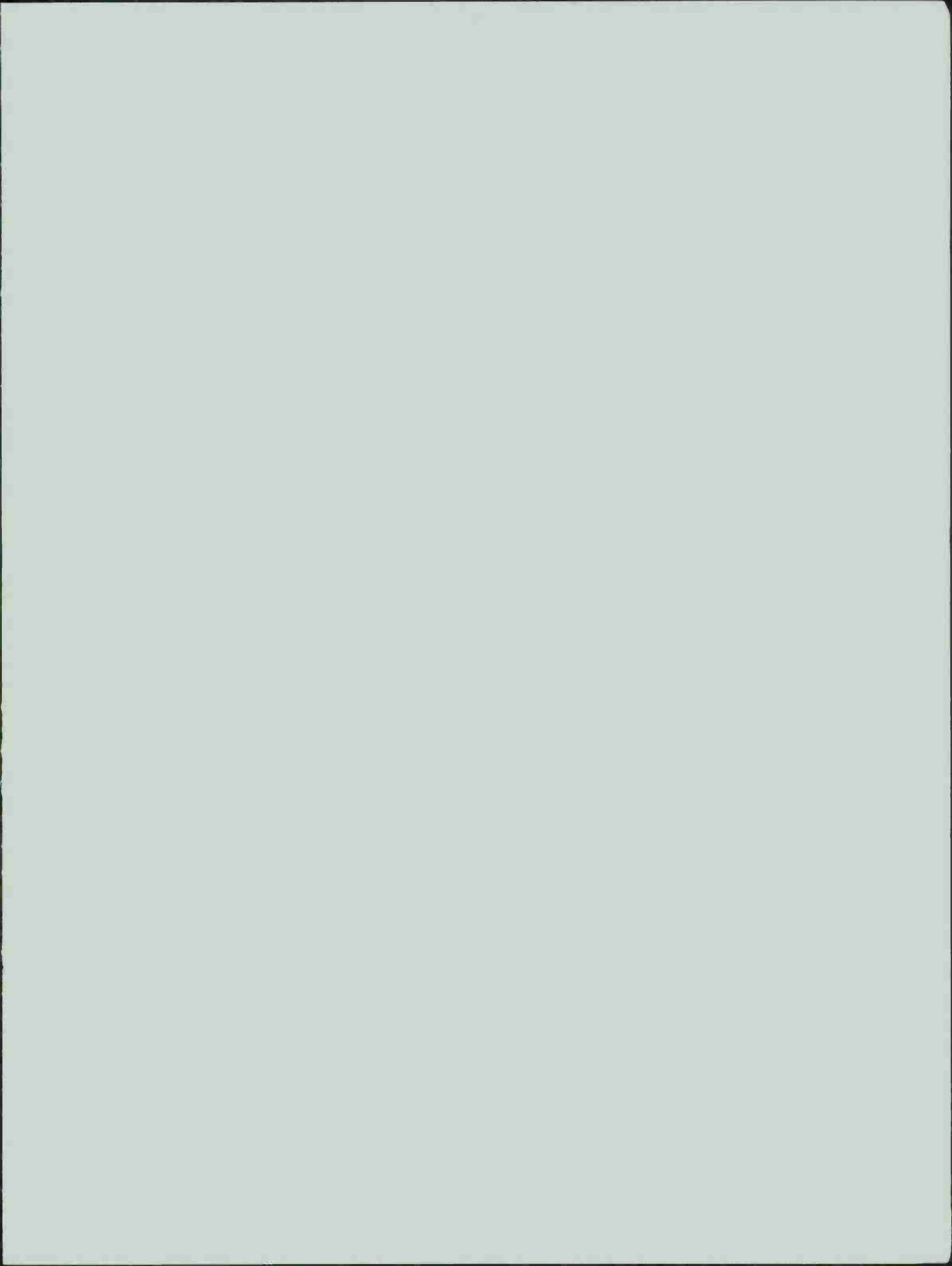
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Czyrklis and Levy

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