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THE EFFECT OF CHLORIDE IONS ON THE
DISSOLUTION BEHAVIOR OF Fe-Ni ALLOYS

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October 1972

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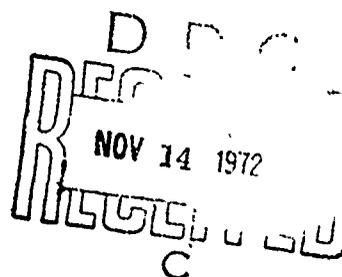
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DALE O. CONDIT, CAPTAIN, USAF

METALLURGY & CERAMICS RESEARCH LABORATORY

PROJECT 7021



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Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) Metallurgy and Ceramics Research Laboratory Aerospace Research Laboratories Wright-Patterson AFB, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP
3. REPORT TITLE The Effect of Chloride Ions on the Dissolution Behavior of Fe-Ni Alloys		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) ARL Technical Report - Internal		
5. AUTHOR(S) (First name, middle initial, last name) Dale O. Condit		
6. REPORT DATE October 1972	7a. TOTAL NO. OF PAGES 22	7b. NO. OF REFS 7
8a. CONTRACT OR GRANT NO. In-House	8b. ORIGINATOR'S REPORT NUMBER(S) ARL TR 72-0124	
b. PROJECT NO. 7021-03-26		
c. DoD Element - 61102F		
d. DoD Subelement - 681306	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES TECH OTHER	12. SPONSORING MILITARY ACTIVITY Aerospace Research Laboratories (LL) Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT The potentiostatic dissolution behavior of Fe-25Ni was studied to determine the effect of (Cl ⁻) ion additions in IN H ₂ SO ₄ at 25 °C. Specimens were dissolved at four potentials in the active and passive ranges and at three (Cl ⁻) concentrations where large changes in dissolution behavior were expected. Current-time behavior, specimen weight change, and solution analysis for Fe and Ni were determined to characterize the dissolution behavior of the alloy. Current-time behavior and post-test surface characterization indicated that pitting occurred at all potentials and (Cl ⁻) concentrations. Atomic absorption analysis for Fe and Ni in the solutions indicated that (1) (Cl ⁻) has no effect in the active dissolution of either component, (2) increases in (Cl ⁻) increase the dissolution of each in the passive range, and (3) no enrichment or preferential dissolution of either component occurred under any exposure condition. The significant role of (Cl ⁻) in the stress corrosion cracking of these alloys would, therefore, seem to be an enhancement of the local dissolution at faults that may exist in the passive film on the alloy.		

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1 NOV 65

I-A

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UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Preferential Dissolution Fe-Ni Alloys Corrosion Polarization Chloride Ions						

I-B

ARL 72-0124

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FOREWORD

This technical report contains the research paper which was presented at the 5th International Congress on Metallic Corrosion held on 21-27 May 1972 in Tokyo, Japan. The research was conducted in the Oxidation and Corrosion Group of the Metallurgy and Ceramics Research Laboratory (ARL) under the supervision of Dr. Henry C. Graham and is part of a program investigating the stress corrosion cracking behavior of alloys of specific importance in aerospace systems.

The author wishes to acknowledge the assistance of those who helped in conducting this research: Mr. John Ankeney and TSgt. James Marshall, who prepared drawings; Mr. Thomas F. Orcutt, who fabricated the specimens; and Mr. Richard Heffelfinger, who provided the solution analyses. The author also wishes to thank Dr. Roger W. Staehle of the Department of Metallurgical Engineering of The Ohio State University for generously providing the alloys being used in these investigations.

INTRODUCTION

Several theories for the mechanism of stress corrosion cracking (SCC) have assumed that dissolution of the alloy is a necessary step in the process. For alloys in the Fe-Cr-Ni system Latanision and Staehle (1) have suggested that Ni enrichment on the surface could be the initial step in the SCC process. Data from Barnartt and vanRooyan (2) and Hoar (3) indicated that such an enrichment process may be occurring. However, other work (4) has shown that very little, if any, enrichment of Ni occurred when Fe-Ni alloys were potentiostatically dissolved in 1N H_2SO_4 solutions at 25°C.

Since the presence of chloride ions (Cl^-) is known to accelerate the stress corrosion cracking of alloys in the Fe-Cr-Ni system, investigations were undertaken to determine the influence of (Cl^-) on the dissolution behavior of these alloys. Potentiodynamic polarization studies (5) were conducted on Fe-25Ni in 1N H_2SO_4 solutions containing from 10 to 10^4 ppm (Cl^-) at 25°C. The results of these studies indicated that the (Cl^-) shifts the cathodic polarization curve in the noble potential direction, had essentially no effect on the active anodic dissolution, and had a pronounced effect on the passive behavior of the alloy as illustrated in Figure 1. The passive character of the alloy was destroyed as the (Cl^-) concentration in the solution was increased above 300ppm.

Using these data as a reference, potentiostatic dissolution experiments were conducted to determine the rates of dissolution of Fe and Ni from the surface of the Fe-25Ni alloy in (Cl^-) environments. The results of this investigation are compared with those reported (4) for the dissolution rates of Fe and Ni in a (Cl^-)-free environment.

EXPERIMENTAL PROCEDURE

All experiments were conducted using high-purity (99.999%Fe and 99.99%Ni) Fe-25Ni alloys. This composition was selected for two reasons. First, its anodic polarization behavior is relatively stable, exhibiting large active current densities, a well-defined passive range with low current densities, and no current oscillations at the active-to-passive transition noted in alloys containing low Ni concentrations (6). Second, this alloy composition is highly susceptible to SCC (7). The cast ingots were hot-rolled, vacuum annealed, and machined into cylindrical specimens approximately 0.2 inches in diameter and 0.5 inches long. These cylindrical specimens were tapped at one end to permit mounting in a modified Sterns-Makrides specimen mount. The specimen surfaces were prepared by abrading through 600 grit SiC abrasive paper and degreasing with acetone. The specimens were weighed before and after the tests to provide comparison with the solution data.

Since the corrosion potential of the alloy is approximately -120 mV(SHE) in all (Cl⁻) solutions(5), the alloy was dissolved at potentials of -20, +80, +180, and +880mV(SHE) in the 1N H₂SO₄ solutions containing 200, 400, or 600 ppm (Cl⁻) [shown as A, B, C, and D in Figure 1]. The test solutions were prepared with distilled water and reagent grade H₂SO₄ and KCl. These particular (Cl⁻) concentrations were selected since the greatest changes in polarization behavior occurred in this range. The potential was maintained using a Wenking 66TS10 Potentiostat. The potential was monitored on a Keithley 610C Electrometer, while the current-time behavior was recorded on a Hewlett-Packard 7001A X-Y Recorder. The time of testing varied from 9 to 330 minutes depending on the magnitude

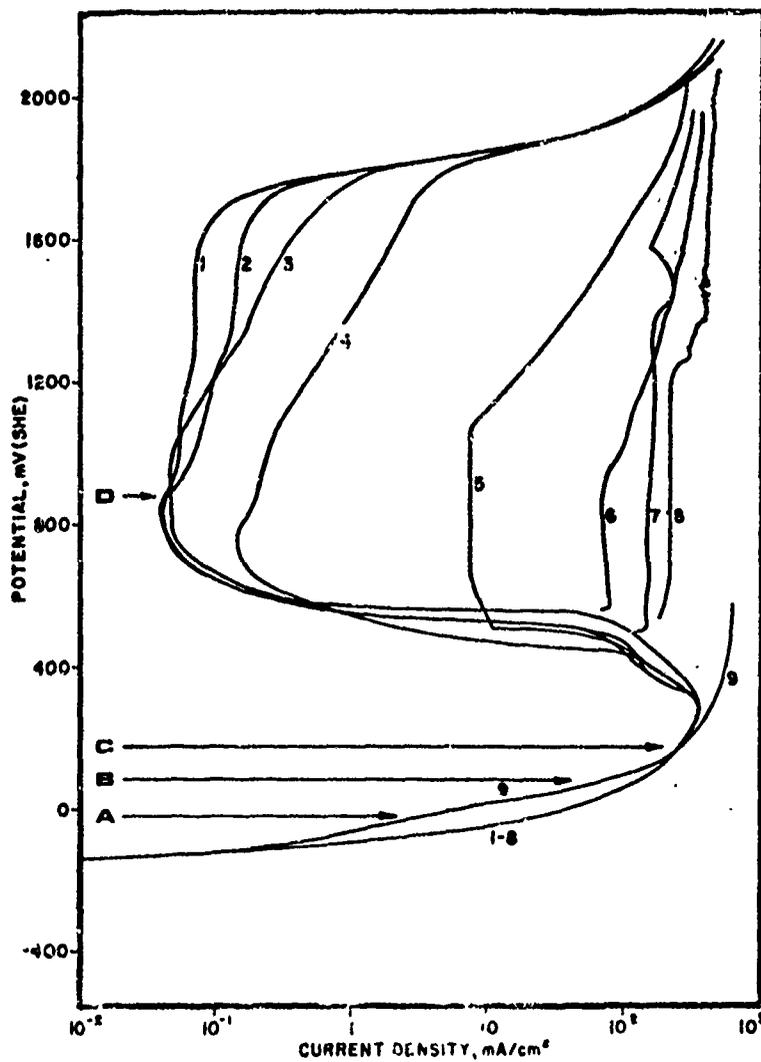


Figure 1. Anodic polarization curves for Fe-25Ni in 1N H₂SO₄ containing (1) 10, (2) 100, (3) 200, (4) 300, (5) 400, (6) 800, (8) 1000, and (9) 10000ppm (Cl⁻) at 25°C.

of dissolution that occurred at each exposure condition.

At selected intervals during each test the potential was removed from the specimen and the solution was stirred by bubbling He gas through it. At this time a 3cc sample was extracted from the solution for analysis. The potential was then re-applied and the test continued. The extracted portions of solution were analyzed using an atomic absorption analyzer. From these data, the rate at which Fe and Ni dissolved from the surface of the alloy was ascertained.

RESULTS AND DISCUSSION

The current-time measurements that were monitored on the X-Y recorder had three general configurations depending on the potential of dissolution (see Figure 2). At low overpotentials ($\eta = 100\text{mV}$) the current steadily increased with time (Figure 2a). At higher overpotentials ($\eta = 200\text{mV}$ and $\eta = 300\text{mV}$) in the active range, the current was relatively constant throughout the entire test (Figure 2b). In the passive range ($\eta = 1000\text{mV}$) the current increased from a low value to a higher value each time the potential was applied (Figure 2c).

At the conclusion of each test the pitting morphology of the specimen was examined by SEM and related to the current-time behavior. Despite the normal appearance of the polarization curves (Figure 1), pitting did occur at overpotentials of 100mV . As more pits were nucleated, the current increased. Since the passive state was not achieved at this overpotential, the pits remained active when the potential was removed. Upon re-applying the potential, the current initially stabilized at a value close to that existing before the potential was removed. Subsequently, the current increased with time as if no interruption had

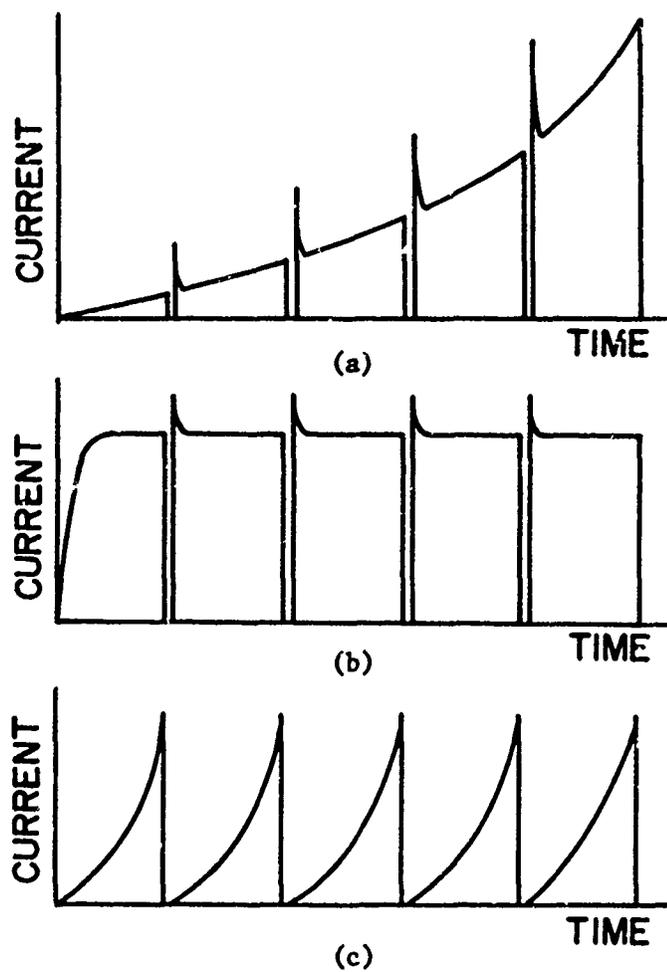


Figure 2. Current-time behavior at (a) low overpotentials, $\eta = 100\text{mV}$, (b) intermediate overpotentials, $\eta = 200\text{mV}$ and $\eta = 300\text{mV}$, and (c) large overpotentials, $\eta = 1000\text{mV}$.

occurred (Figure 2a). The specimens dissolved at overpotentials of 200 and 300mV were uniformly and grossly dissolved, providing a constant current for the entire test (Figure 2b). In the passive range, pits that formed initially were repassivated when the potential was removed. These pits, or others, were then re-initiated each time the potential was re-applied, manifesting the observed current-time behavior (Figure 2c).

The specimen weight changes, the integrated current-time weight change calculations, and the atomic absorption analyses were all relatively comparable. The integrated current-time weight change data was always within 6% of the measured weight change and the average difference was 3%. The comparison of the atomic absorption analyses with the measured weight change was less favorable, with one difference being 19% and the average 11%.

The concentration-time curves obtained from the atomic absorption analyses are shown in Figures 3-5. These results have been plotted on a logarithmic scale because of the wide ranges of concentrations and times. A linear regression analysis was conducted on the curves in the same manner as in the previous investigation (4). The slopes of the curves that were obtained from the regression analyses were substituted into the following equation to obtain an intrinsic rate constant for Fe and Ni:

$$K_i = \frac{M_s}{AM_i} \left(\frac{\partial c_i}{\partial t} \right) \times 10^{-6}$$

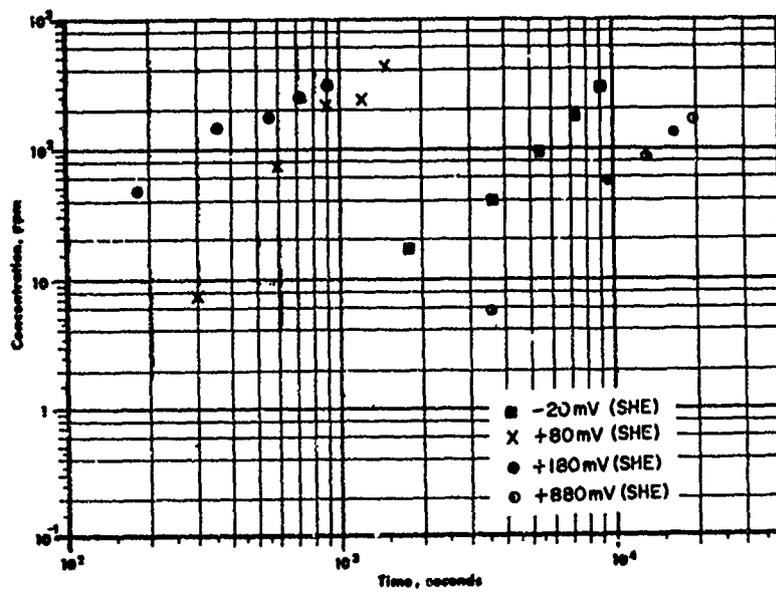
where K_i = intrinsic rate constant, moles/cm²·s

M_s = mass of the solution, gms

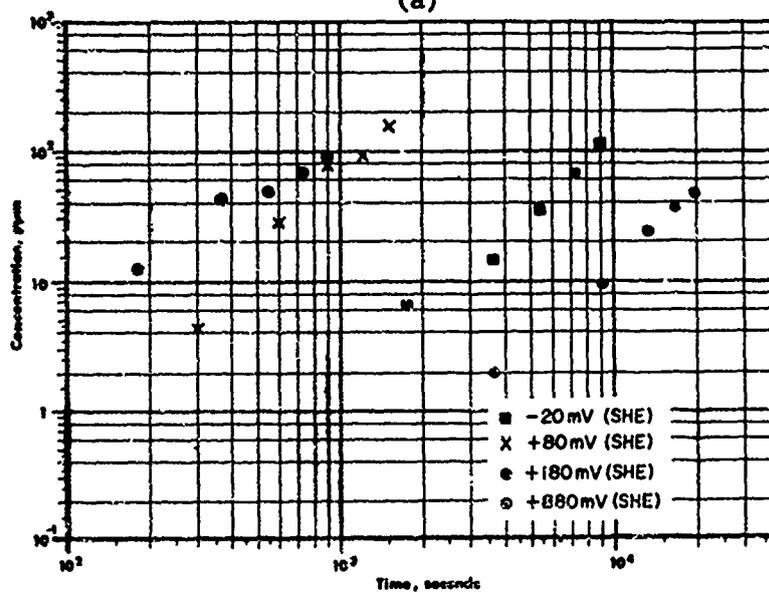
A = area of the specimen, cm²

M_i = mass of Fe or Ni, gms

$\partial c_i / \partial t$ = slope of concentration-time curve, ppm/s

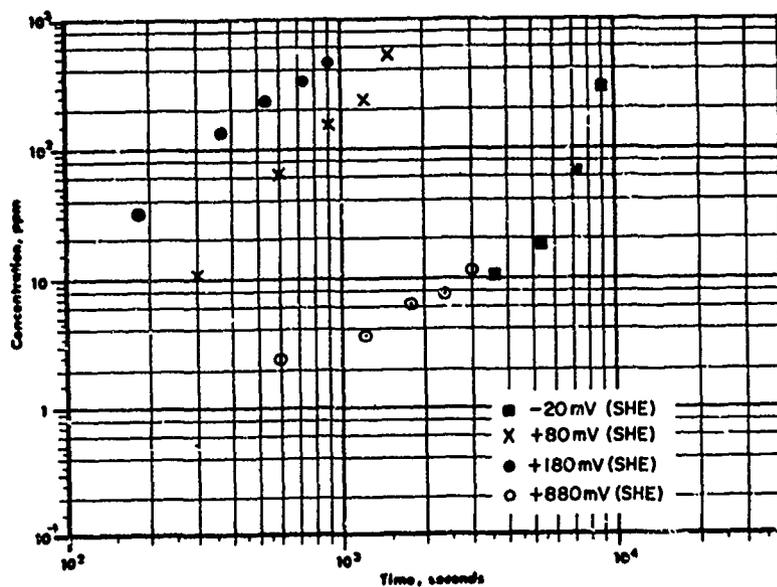


(a)

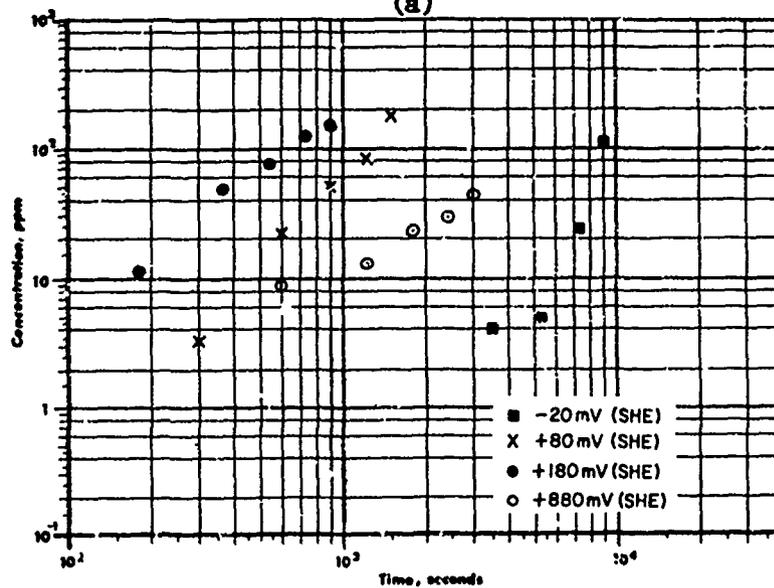


(b)

Figure 3. Concentration of (a) Fe and (b) Ni in solution as a function of time at given potentials in 1N H₂SO₄ containing 200ppm (Cl⁻) at 25°C.

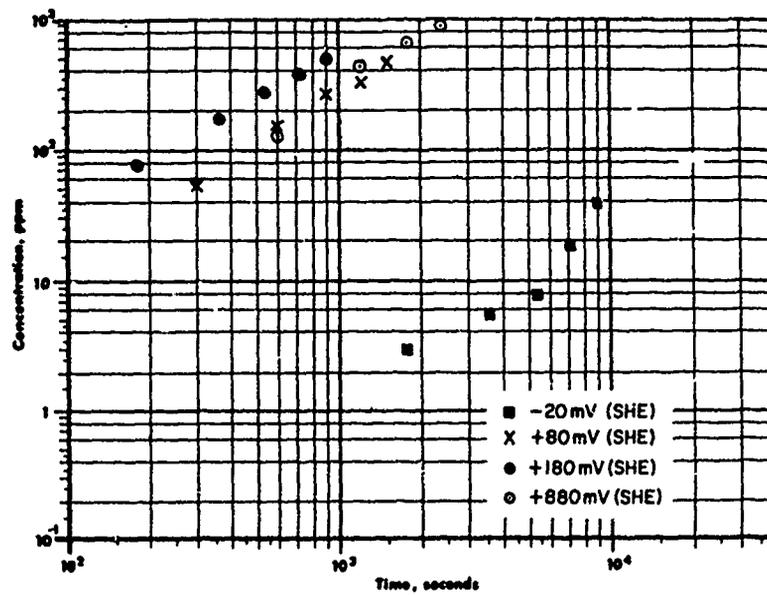


(a)

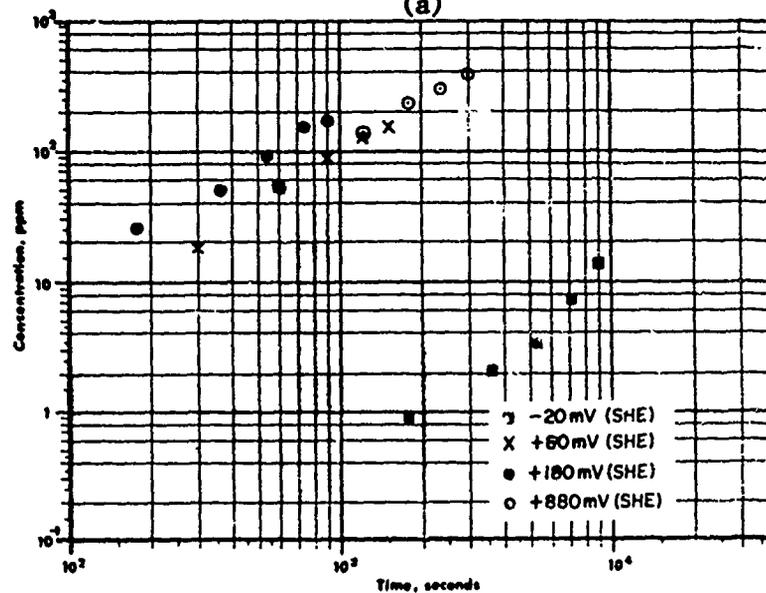


(b)

Figure 4. Concentration of (a) Fe and (b) Ni in solution as a function of time at given potentials in 1N H₂SO₄ containing 400ppm (Cl⁻) at 25°C.



(a)



(b)

Figure 5. Concentration of (a) Fe and (b) Ni in solution as a function of time at given potentials in 1N H₂SO₄ containing 600ppm (Cl⁻) at 25°C.

A more accurate comparison of K_{Fe} and K_{Ni} was obtained by normalizing both constants to obtain $K_{Fe,n}$ and $K_{Ni,n}$; this was accomplished by dividing K_{Fe} and K_{Ni} by their respective percentages of Fe and Ni in the alloy.

The values of K_i and $K_{i,n}$ are given in Table I. When these data are compared with those of the previous work (4), they show excellent correlation. The normalized rate constants for Fe and Ni at $\eta = +120\text{mV}$ in (Cl^-) -free environments were 3.6×10^{-7} and 2.3×10^{-7} moles/cm²·sec., respectively. The interpolated values for both of these constants in (Cl^-) -containing environments average 1.15×10^{-7} moles/cm²·sec. The data in Table I indicate that for a given (Cl^-) concentration, the rates of dissolution of Fe and Ni increase with potential in the active range and decrease when the passive state is achieved. Second, the data show that the individual dissolution rates in the active range [-20, +80, and +180mV(SHE)] are unaffected by changes in the (Cl^-) concentration; whereas, in the passive range these dissolution rates are significantly increased by increases in the (Cl^-) concentration. These increases in dissolution suggest that local dissolution within pits or cracks in a passive film where (Cl^-) can concentrate may be exceedingly high causing rapid growth of these faults. Finally, and most important, the normalized rates of dissolution of Fe and Ni from the surface of the alloy are nearly equal. The Fe/Ni ratio, in other words, is nearly always 3.0; this is shown in Figures 6-8 where the Fe/Ni ratio in the solution is calculated for each data point. These data indicate that neither component is preferentially dissolving and that no appreciable enrichment of Ni is occurring on the surface.

TABLE I.
 Intrinsic Rate Constants for Fe and Ni
 in 1N H₂SO₄ Containing (Cl⁻) Ions.

(Cl ⁻), ppm	E, mv(SHE)	$k_{Fe} \times 10^8$ moles/cm ² -sec	$k_{Ni} \times 10^8$ moles/cm ² -sec	$k_{Fe,n} \times 10^8$ moles/cm ² -sec	$k_{Ni,n} \times 10^8$ moles/cm ² -sec
200	- 20	5.42	1.85	7.23	7.39
200	+ 80	44.3	15.9	59.1	63.6
200	+180	61.5	23.1	82.0	92.4
200	+880	2.29	0.63	3.05	2.52
400	- 20	6.78	2.24	9.05	8.95
400	+ 80	62.6	21.9	83.4	87.6
400	+180	90.7	30.4	121.	122.
400	+880	6.53	2.20	8.71	8.80
600	- 20	0.81	0.28	1.09	1.14
600	+ 80	48.1	15.6	64.1	62.4
600	+180	88.2	28.5	118.	114.
600	+880	76.3	24.2	102.	99.6

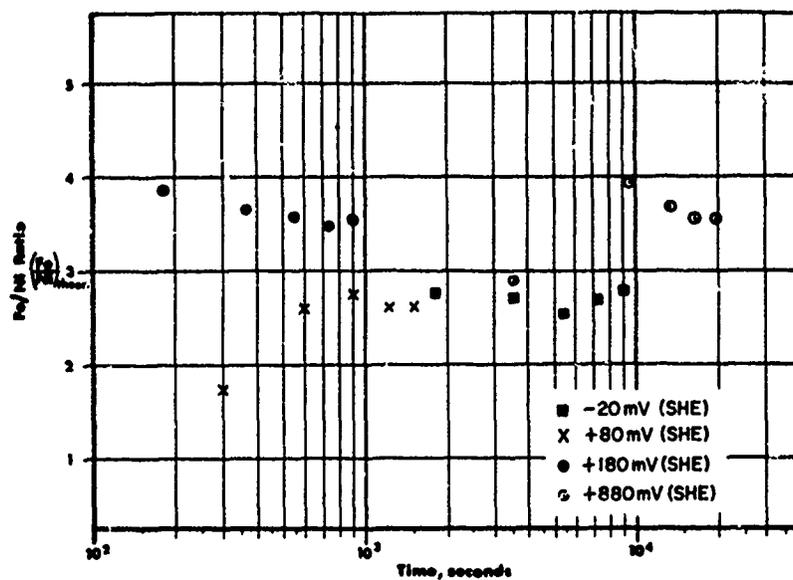


Figure 6. Fe/Ni ratios in solution for given potentials in 1N H₂SO₄ containing 200ppm (Cl⁻) at 25°C.

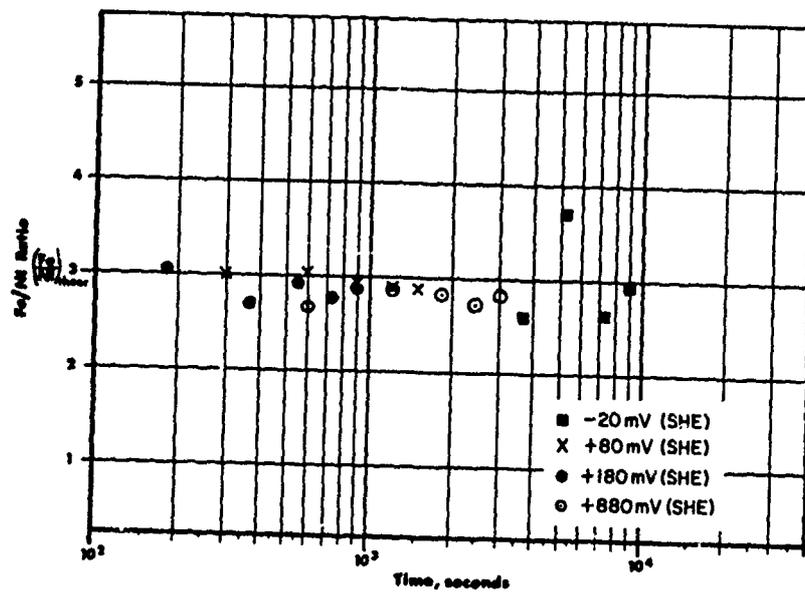


Figure 7. Fe/Ni ratios in solution for given potentials in 1N H₂SO₄ containing 400ppm (Cl⁻) at 25°C.

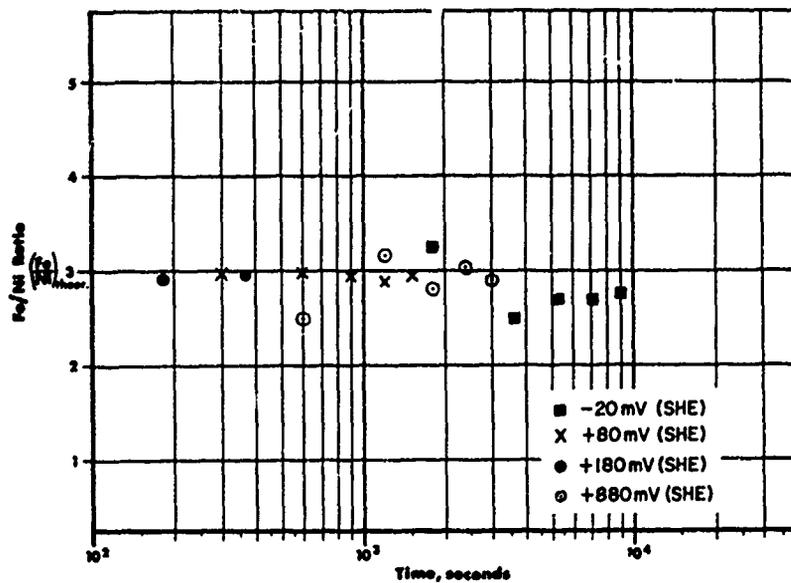


Figure 8. Fe/Ni ratios in solution for given potentials in 1N H₂SO₄ containing 600ppm (Cl⁻) at 25°C.

CONCLUSIONS

The following conclusions can be drawn from this research:

1. (Cl^-) has no effect on the active dissolution of Fe and Ni from the Fe-25Ni alloy in 1N H_2SO_4 .
2. Increases in the (Cl^-) concentration increase the dissolution of both Fe and Ni in the passive range.
3. Pitting occurs at both high and low overpotentials in all (Cl^-) concentrations.
4. No enrichment of Ni occurs on the surface of this alloy, regardless of the (Cl^-) concentration and overpotential.
5. The most likely role that (Cl^-) ions play in the SCC of these alloys is to enhance local dissolution at nucleated pits where the (Cl^-) ions may concentrate.

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