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Corrosion Resistance of Nitrided Low-Alloy Steels

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mA/cm^2	milliampere per square centimeter
h	hour	mV	millivolt
in	inch	mV/min	millivolt per minute
μm	micrometer	min	minute
μm/yr	micrometer per year	V	volt
mA	milliampere	wt %	weight percent

CORROSION RESISTANCE OF NITRIDED LOW-ALLOY STEELS

By John V. Scalera [1]

ABSTRACT

Because of U.S. dependency on imported critical metals, the Bureau of Mines has conducted research to evaluate the possible substitution of nitrided low-alloy steels for higher chromium-containing alloys. The corrosion data for nitrided steels are limited primarily to the Soviet literature. The objective of this study was to determine the corrosion properties of six commercially nitrided low-alloy steels in a 5-wt % NaCl solution at pH 4. Weight-loss tests indicated that, in deaerated test solutions, most of the nitrided steels were less corrosion resistant than nontreated steels. However, electrochemical tests indicated that under more oxidizing conditions, nitrided materials are converted to a passive state with a significantly reduced corrosion rate. Electrochemical tests performed in an aerated environment confirmed the passivity of the samples in an oxidizing environment.

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INTRODUCTION

Within the past 20 years, nitriding has become useful as a heat-treatment technique for improving the surface properties of finished steel products. Some of the observed benefits of nitriding have been increased case hardness, increased fatigue and wear resistance, and low material distortion. Limited testing by industry has indicated some improvement in the corrosion resistance of certain types of steels. The expanding use of nitrided steels, in particular by the automobile industry as substitutes for higher chromium-containing alloys indicates confidence in the corrosion resistance of nitrided steels.

The steel gas nitriding process involves the heating of steel to a temperature below the austenitic transformation (i.e., from 495° to 580° C) in an atmosphere of anhydrous ammonia or a hydrogen and nitrogen mixture. Sometimes a gaseous hydrocarbon is also used in the atmosphere. The finished products typically have a fine surface layer of ferric nitrides ranging in thickness from about 2 to 50 μm. This surface layer consists of several forms of iron nitrides, the most abundant forms being ε nitride ($Fe_{2-3}N$) and γ nitride (Fe_4N). Because of its white appearance, it is often referred to as the white layer (fig. 1).
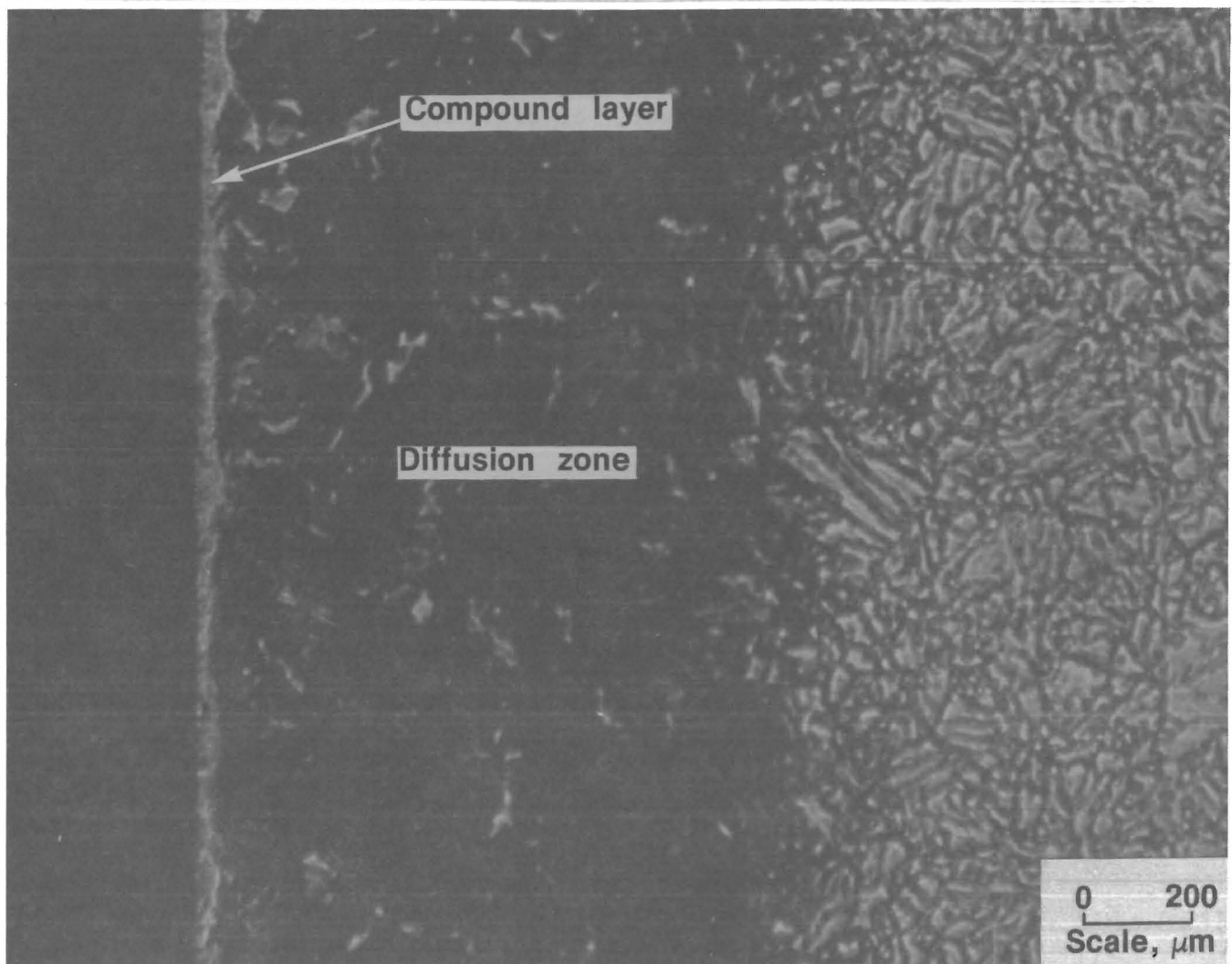

FIGURE 1. - Cross section of an ion-nitrided type A387-22 steel. The compound layer is approximately 20 μm thick; the diffusion layer is several hundred micrometers thick (3% nital, X 100).

Below the ferric nitride layer lies a diffusion layer of up to several hundred micrometers. Here, nitrogen can be found in atomic form along with iron nitrides and nitrides of some of the other possible substrate alloying constituents such as chromium, aluminum, and molybdenum.

This report presents a brief literature review of nitrided materials and their performance in corrosive environments. Results are also presented from corrosion testing of low-alloy nitrided steels in deaerated 5-wt % NaCl solution conducted by the Bureau of Mines.

DEVELOPMENT OF STEEL NITRIDING TECHNOLOGY

In 1908, Adolph W. McClef applied for a patent on a process by which iron and steel articles were heated from 482° to 982° C (900° to 1,800° F) in a retort with an anhydrous ammonia atmosphere. The resultant product was a very dull silver-colored coating on the metal. The coating was described as being "hard..., extremely reluctant to tarnish, corrode, rust, or oxidize" (1).[2]

In 1924, Adolph Fry was granted a patent involving the nitriding process (1). In his process, hardened steel alloys that contained aluminum, chromium, manganese and/or silicon were hardened by exposure to anhydrous ammonia at approximately 580° C. The use of lower nitriding temperatures resulted in a deeper, more stable case formation that was less prone to peeling. The use of nitride-forming alloy constituents, such as aluminum and chromium, in the steel matrix was found to increase hardness without decreasing the stability of the nitrided case at elevated temperatures (1,000° C) (2). Because the case-hardening technique (carburizing) in use at the time of the Fry patent (1) required higher energy cost due to higher temperatures, regrinding of surfaces to meet final specifications, and sometimes product rejection due to excessive deformation, the findings of Fry were very attractive to the commercial world of steel heat treating. From Fry's work, a series of nitriding steels evolved containing from 1.3% to 1.8% Cr and 1.0% to 1.3% Al (2). Because brittleness was encountered with nitrided steels containing chromium and aluminum,

molybdenum was later added for increased strength (1).

NITRIDING TECHNIQUES

Various techniques of nitriding have been developed since the initial gas nitriding work. The Floe process (3) is a two-stage gas nitriding process. The Floe process greatly reduces the thickness of the brittle white layer of iron nitrides formed by the single-stage nitriding process. The first stage of the Floe process is similar to single-stage gas nitriding where the sample is nitrided using ammonia gas dissociated to almost 30% at temperatures of 495° to 525° C. The second stage, using ammonia gas dissociated from 65% to 85%, significantly reduces the white layer built up in the first stage (3). Reduction in the thickness of the white layer is important in applications where spalling of the white layer during service could lead to accelerated wear or seizure of mechanical parts.

Liquid nitriding uses a cyanide salt bath to supply the source of nitrogen. The process has shown greater success in nitriding carbon steels than has been exhibited by the gas nitriding techniques (4). A unique variation of the liquid nitriding process is the Melonite QPQ process,[3] developed by the Degussa Corp.[4] of West Germany (5). The process

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[2]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

[3]Reference to specific processes or products does not imply endorsement by the Bureau of Mines.

[4]Within the United States, the Kolene Corp., Detroit, MI, has the exclusive rights for the marketing and licensing of the process.

involves immersion of the workpiece in a liquid nitriding bath of cyanide salts at 550° C for about 90 min, followed by immersion in an oxidizing molten salt bath at 343° to 399° C for about 20 min. After the oxidizing bath, a mechanical lapping is done with 1/8- to 3/16-in-diameter abrasive Al_2O_3 chips. Workpieces are placed in a vibratory bowl with the Al_2O_3 chips for 20 min at a fixed vibratory amplitude and frequency. This lapping is needed to remove the rough appearance of the oxidized sample. After the lapping, the sample is placed back into the oxidizing bath for another 20 min. The final product has a shiny black surface, which is claimed to have very high hardness with excellent corrosion resistance (5). The oxidizing bath was initially developed for environmental reasons as a method to oxidize cyanide waste.

Ion nitriding (or glow-discharge nitriding) involves a chamber that acts as an anode (positive electrode), with the workpiece being the cathode. A gas mixture of nitrogen, hydrogen, and sometimes hydrocarbons, is bled into the evacuated chamber. A potential of several hundred volts between the cathode and anode ionizes the atoms in the chamber. The cations move toward the cathode forming both stable and unstable nitrides and, in the process, elevate the temperature of the workpiece. During the process, the unstable nitrides decomposed releasing nitrogen, which can then partly diffuse into the workpiece. Ion nitriding has several advantages (6–8) over gas and liquid nitriding, including the following:

1. Lower nitriding temperature (315° to 649° C) prevents structure transformation in steels and subsequent hardness loss.

2. Less gas required.

3. Shorter process times for development of white layer and diffusion zones.

4. Fewer environmental problems because neither ammonia or toxic cyanide salts are used.

5. Excellent control of processing variables (voltage, temperature, gas composition, and pressure), so as to obtain the desired white layer composition, and thickness.

6. Low cost involved in masking workpiece areas.

7. Sputtering techniques can be used to clean sample surface prior to nitriding.

With the refinement of these techniques, a large array of steels (3) have been successfully nitrided yielding improved performance in the areas of increased surface hardness, wear resistance, fatigue life, and corrosion resistance (low-alloy and carbon steels). Steels that have been successfully nitrided include carbon steels, low-alloy steels, and tool steels, as well as ferritic, martensitic, and austenitic stainless steels. For the low-alloy steels, the nitride-forming elements Cr, Al, and Mo are commonly used (3). Chromium additions increase the ductility of the nitrided surface. Aluminum nitride, one of the most stable of all nitrides, yields increased hardness and wear resistance. Molybdenum reduces the brittleness of the nitride surface at elevated temperatures. Other alloying elements found in nitridable steels are vanadium and titanium. In most nitriding steels, carbon in the substrate has been limited to levels below 0.5 wt %. This limitation is required because the formation of ferric carbides below the surface inhibit the diffusion of nitrogen into the substrate, decreasing the effective depth of nitriding.

Surface nitriding techniques have been used commercially worldwide. Industry has used nitriding processes to improve performance and cut cost on parts such as

camshafts, crankshafts, cylinder heads, differential housings, intake and exhaust valves, transmission gears, etc. (9). Japan nitrides 5 million engine valves monthly (10). In West Germany, nitriding has been used successfully to replace chrome-plated shafts in excavators resulting in a considerable cost savings (9). Other uses of nitriding have been the improved performance of gears and shafts used in a variety of pumps.

PREVIOUS CORROSION STUDIES

Much of the research on the corrosion resistance of nitrided steels has been conducted in the Soviet Union, with a large percentage of these studies being concerned with high-alloyed materials such as 13% and 18% Cr stainless steels and the carbon steels. Bil'Chenko and Permyakov (11) reported that conventional nitriding temperatures of 495° to 580° C reduce the corrosion resistance of stainless steels because of the depletion of chromium out of solid solution as precipitates of CrN and $(CrFe)_7C_3$. Such findings are in agreement with other literature (3, 7). Bil'Chenko and Permyakov (11) studied the effect of nitriding temperatures from 550° to 1,050° C on the types of nitrides formed and their corrosion resistance. At 550° C (close to conventional nitriding temperatures), a matrix of $Fe_{2-3}N$, Fe_4N, and Cr nitrides were formed; whereas, at 1,050° C, chromium nitrides were the only nitrides formed. The higher temperature (1,050° C) and shorter nitriding process times produced products showing greater corrosion resistance than those prepared at the lower conventional nitriding temperature (550° C). Bil'Chenko and Permyakov (11) conclude that although surface ferric nitrides increase the corrosion resistance of plain carbon and low-alloy steels, these nitrides can lead to a reduction of corrosion resistance in stainless steels, and they attribute the reduction in corrosion resistance to the formation of galvanic cells in the heterogeneous surface of the nitrided layers.

Reportedly, alloy additions of 0.5% Ti, 1.5% Al improved the corrosion

resistance of nitrided 12% to 14% Cr steels in 1N H_2SO_4 (12). Varhoshkov and Sedloev (13) evaluated the corrosion resistance of ion-nitrided, low-alloy steels (0%, 1%, and 5% Cr) in aerated solutions of 0.1N Na_2SO_4, 0.1N NaCl, and 0.1N sulfuric acid. Using an ion-nitriding process, they formed specific nitrides on the surface of each steel type, homogeneous Σ nitride, homogeneous γ' nitride, or a heterogeneous surface of Σ and γ' nitrides. Potentiodynamic polarization tests were used to determine which type of nitrided surface gave the best corrosion resistance. Unfortunately, pitting evaluations were not performed. Conclusions were as follows (13):

1. The heterogeneous phase of Σ and γ' nitrides showed the maximum corrosion resistance in comparison to monophase nitrided layers.

2. The corrosion behavior of nitrided low-alloy steels is unsatisfactory in a 0.1N sulfuric acid electrolyte.

3. Nitriding increases the corrosion resistance of low-alloy steels in neutral electrolyte solutions of 0.1N Na_2SO_4 and 0.1N NaCl.

In contrast to the findings of Varhoshkov and Sedloev (13), Edenhofer (7) reports that a Σ nitride monophase maximizes corrosion resistance in low-alloy steels. In reference to Edenhofer's findings, one would suspect the homogeneously nitrided case would have greater corrosion resistance in comparison to the heterogeneously nitrided case owing to the reduced potential for galvanic cell formation and mechanical stress due to varying crystal types in the case.

Several reports on low-carbon steels concluded that increased corrosion resistance can be imparted by nitriding. Tests include tapwater immersion test, open-circuit monitoring in flowing tapwater and 3% NaCl (14), and salt spray tests (4, 15). Hendry (16) reported improved oxidation resistance of nitrided mild steels in simulated boiler flue gas

atmospheres. Jack (17) found improved oxidation resistance of nitrided ferric iron alloys.

Because of the potential of nitrided low-alloy steels substituting for stainless and chromium-plated steels, there is a need for more extensive experimentation. Electrochemical and immersion weight-loss tests were designed to evaluate corrosion resistance of the nitrided low-alloy and carbon steels. The steel types selected represent a cross section of commercially available steels with varying low quantities of chromium and/or nickel. Nitralloy 135-modified (a carbon-steel containing 1% to 2% Cr, 1%

Al) was developed in the United States specifically as a nitriding steel. The 410 SS was selected for relative comparison of corrosion performance. Coupons from weight-loss tests used to obtain corrosion rates were examined by optical techniques to identify the type of corrosion. Electrochemical data provided information about the passivating potential of the sample in a 5-wt % NaCl solution. An acidic chloride solution was chosen because of the known corrosion problems associated with chlorides and acidic environments on steels used industrially and by the general public. The test solutions were deaerated to elimate the effect of oxygen as a variable.

EXPERIMENTAL PROCEDURE[5]

SAMPLE PREPARATION

Coupon Preparation

Table 1 lists the crystallographic structure and composition of the six commercial steels used in this study: types 1020, 4130, 4817, A387-22, Nitralloy 135-modified (135-mod), and 410 stainless. Two forms of coupons were used: square plates 3/4 in by 3/4 in by 1/16 in or discs 1 in diameter by 1/8 in thick. All of the coupons were ground to a 320 grit finish and, except for the 410 SS, were stress relieved at 600° C for 1 h, and oxides were removed with a 0.05 μm, Al₂O₃

powder. The 410 SS coupons were stress relieved at 680° C for 1 h and then at 600° C for 1 h. The 410 SS coupons were heat treated differently to allow for a homogeneous distribution of carbides. By evenly distributing the carbides during nitriding, a more uniform nitride case with inherently lower residual stress would be obtained as compared to a coupon undergoing a single treatment at 600° C.

Nitride Treatment[6]

The coupons were commercially nitrided by one of three techniques: two-stage gas nitriding (Floe process); ion

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[5]Essential data and technical assistance in the design of the experiment were provided by Stephen Chalk, engineering technician, Bureau of Mines, Avondale Research Center (now chemical engineer, Naval Ordnance Station, Indian Head, MD).

[6]The Bureau of Mines acknowledges the exchange of information concerning ion-nitrided materials with James Conybear of Midland Ross Corp. of Columbus, OH, and the MLN-treated materials by James Easterday of the Kolene Corp., Detroit, MI.

TABLE 1. - Structure and concentration of alloying elements in six experimental steels, weight percent

Steel type	Structure	Al	C	Cr	Mn	Mo	Ni	P	S	Si
1020...	Ferrite-pearlite	0.05	0.20	0.015	0.15	ND	0.015	ND	0.050	0.005
4817...	Martensite......	ND	.19	ND	.62	0.22	3.33	0.008	.024	.28
4130...	Ferrite-pearlite	ND	.29	1.04	.53	.16	ND	.010	.022	.24
135-mod	...do...........	1.03	.41	1.60	.61	.22	.16	.010	.015	.32
A387-22	...do...........	ND	.08	2.24	.44	.93	ND	.019	.013	.24
410 SS.	Martensite......	ND	.15	12.5	.50	ND	ND	.020	.015	.50

ND Not determined.

(glow-discharge) nitriding; and liquid nitriding (Melonite QPQ process), which will be referred to as the "MLN" process throughout the remainder of this paper. The surfaces of the coupons created by the Floe process were nonhomogeneous with some scaling and iron oxide formation. X-ray diffraction revealed the coupons to have a very thin compound layer and confirmed the presence of iron oxides. Because of their inconsistent surface appearance, the coupons treated by the Floe process were not evaluated extensively. However, it was felt that the surface treatment these coupons received was not representative of the product that should result from the Floe process and other gas nitriding facilities. Unfortunately, no further gas-nitrided coupons were obtained prior to the termination of this study.

TEST PARAMETERS

The test solution was 5-wt % NaCl, adjusted to a pH of 4 with HCl and maintained at $25°$ C$\pm1°$. With the exception of a few aerated tests, all the test solutions were deaerated using nitrogen. To assess the corrosion resistance of the treated steels, electrochemical and surface characterization techniques plus immersion weight-loss tests were used. Electrochemical measurements included open-circuit potential monitoring over a 1-month period and potentiodynamic polarization tests.

WEIGHT-LOSS TESTS AND SURFACE CHARACTERIZATION

Coupons were immersed in a deaerated 5-wt % NaCl solution, pH 4, for 1 month. Corrosion rates were calculated from the weight loss data on the assumption that uniform corrosion was responsible for a high percentage of the weight loss. Surfaces were characterized using X-ray diffraction, metallography, optical microscopy, and scanning electron microscopy techniques before and after sample testing. X-ray diffraction data were used to determine the composition of the first few micrometers of the white layer distinguishing between Fe_3N and Fe_4N nitrides as well as minor compounds. Metallographic examination of polished cross sections gave values for the thickness of the white layer. Microscopic techniques were used to determine the extent and forms of corrosion taking place: uniform corrosion, localized corrosion in the form of pitting, and exfoliation, where there is descaling parallel to the surface.

ELECTROCHEMICAL TESTS

Open-Circuit Potentials

Open-circuit potentials were obtained by using a polycarbonate sample holder which exposed approximately 2 cm^2 of the sample. A stainless steel shaft, protected by a polycarbonate sheath, contacted the perimeter of the sample. The open-circuit potentials (E_{oc}) were monitored for 1 month. The collected data gave an indication of stability or deterioration of surface films during the 1-month immersion period. Direct comparisons of E_{oc} and corresponding E_o values would also indicate passive film formation in cases where E_{oc} values were positive to E_o values. E_o, or the zero current potential, is the potentiodynamic polarization test potential where the net value of the combined anodic and cathodic currents is equal to zero.

Potentiodynamic Polarization

Potentiodynamic polarization tests were run starting from a potential of -1,000 mV versus the standard calomel reference electrode (SCE), at a rate of 10 mV/min in the anodic direction. Tests were terminated when the current density exceeded 50 mA/cm^2. The potentiodynamic test indicates change in current density versus change in applied potential. This test provides information on the electrochemical performance of the sample, indicating active, passive, and

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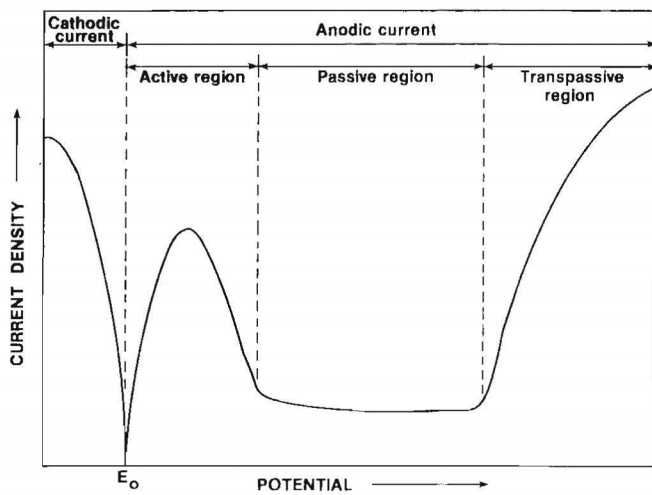
FIGURE 2. - Typical anodic dissolution behavior of active-passive metal.

transpassive regions, and its zero current potential (E_o), the experimentally observed potential where the net value of the combined anodic and cathodic currents is zero. (See figure 2.) Passivation regions are ranges of potentials where the current density and, in turn, corrosion rate are reduced because of the formation of a protective surface film which inhibits dissolution (18). At potentials more positive than the passive region, this film may deteriorate, resulting in a large increase in current density. This region is known as the transpassive region. If the E_o lies in the passive region, the metal will often exhibit lower corrosion rates than when the E_o lies outside of any passive region.

FIGURE 3. - "Bubble" defects typically found on surface of 410 SS coupons treated by MLN process (3% nital, X 100).

EXPERIMENTAL RESULTS AND DISCUSSION

SURFACE CHARACTERIZATION

The ion-nitrided coupons had a soft matte finish consisting of fine crystals extending perpendicularly from the surface. Below the white layer, the nitrided metal ranged in color from a "brassy" gold to a solid black. In contrast to the ion-nitrided coupons, the MLN-treated coupons appeared fairly homogeneous in color with shades ra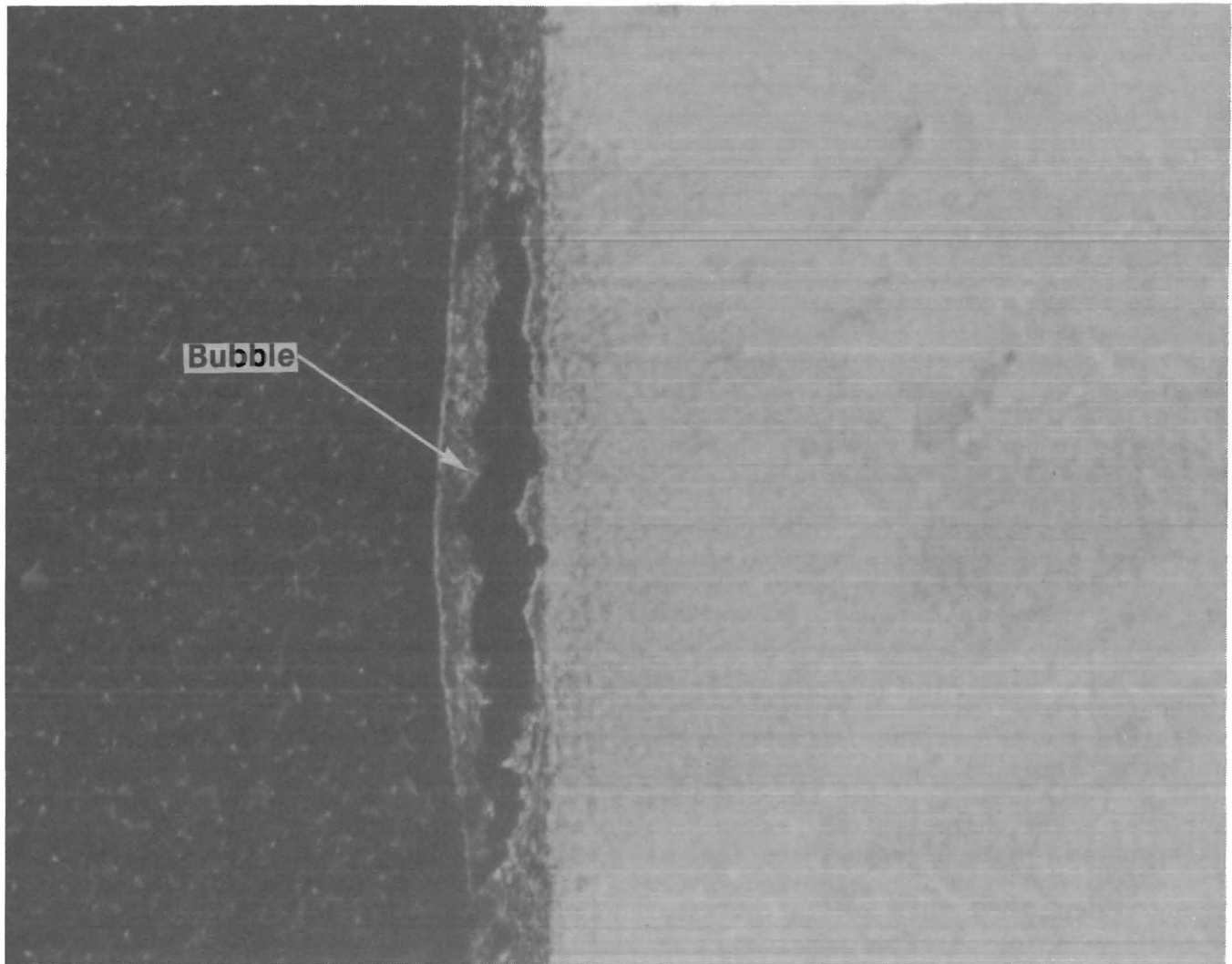nging from a brown-black for carbon steels to a solid black color for the 410 SS. The surfaces were smooth and had a metallic luster. All the 410 SS coupons treated by the MLN process had surface defects in the form of "bubbling," as shown in the cross sectional view in figure 3. These defects may be the result of high stress caused by the formation of complex iron and chromium carbide and nitride structures (11).

Table 2 lists the various types of compound layers and their thickness as measured on the test coupons. The MLN coupons, with the exception of the 410 SS, had a fairly consistent compound layer thickness of 13 to 15 μm. The MLN-treated 410 SS coupons had only a 3-μm-thick compound layer. The reduction in thickness can be attributed to the formation of chromium nitrides on the surface of the coupons, which would restrict the penetration of nitrogen further into the substrate. The ion-nitrided coupons ranged in compound layer thickness from 6 to 21 μm, depending on the steel. With the exception of the 410 SS, the greater the chromium content of the ion-nitrided steels, the greater the compound layer thickness. The ion-nitrided 410 SS, as in the case of the MLN-treated 410 SS coupons, probably forms a dense network of chromium nitrides on the surface, which limits the further penetration of nitrogen into the substrate. Both the ion-nitrided and MLN-treated coupons had varying compound layer compositions, depending on the steel type, homogeneous Σ or γ' or a heterogeneous mixture of Σ and γ'. Low concentrations of magnetite were also detected in the MLN coupons. Coupons of the same steel type and that underwent the same nitriding treatment

TABLE 2. – Compound-layer thickness and surface consitiuents of nitrided layers[1]

Steel type	Treatment[2]	Compound-layer thickness, μm	Surface constituents[3]		
			$Fe_{2-3}N$	Fe_4N	Magnetite
1020......	L	14	M	M	Lw
	I	8	M	M	ND
4817......	L	13	M	Mn	Lw
	I	6	Mn	M	ND
4130......	L	15	M	ND	Mn
	I	14	Lw	M	ND
135-mod...	L	14	M	Mn	Mn
	I	19	M	M	ND
A387-22...	L	15	Mn	M	Lw
	I	21	Lw	M	ND
410 SS....	L	3	M	Mn	Mn
	I	10	M	Mn	ND

[1]Composition data based on X-ray diffraction; quantitative ranges based on relative comparison of peak heights; thickness based on metallography.
[2]I Ion nitrided. L MLN processed.
[3]Lw Low levels detected, <10% of sample; Mn Minor constituent, 10% to 45% of sample; M Major constituent, >45% of sample; ND Not detected.

invariably were found to have the same surface composition, based on the similarity of the X-ray diffraction patterns. It must be noted that the X-ray diffraction technique used to obtain the compound zone composition was only capable of analyzing the first few micrometers of the compound zone. Variations below the initial surface layer would not be detected by X-ray analysis.

WEIGHT-LOSS TESTS

Tables 3 and 4 present the corrosion rate values obtained from the weight-loss data. Table 4 reports the results of these weight-loss tests in order of decreasing equivalent corrosion rate. Because only a single measurement period was used, it was not possible to determine if these rates were time dependent.

General trends showed the nontreated coupons to have lost the least amount of weight, and the MLN-treated coupons lost the greatest amount of weight. Of the steels tested, the nickel-containing type 4817 was by far the least corrosion resistant of all the steels when considering both nitrided and nontreated forms. The 1020 nitrided coupons also exhibited large weight losses, but their nontreated counterparts were some of the most corrosion resistant.

In most cases, the ion-nitrided coupons showed less weight loss overall than did the MLN-treated coupons, but only the ion-nitrided 135-mod coupons showed significantly less weight loss than their nontreated counterparts. From the weight-loss tests, one might conclude that the corrosion resistance in

TABLE 3. – General corrosion rates of six nitrided and nontreated steels in deaerated 5-wt % NaCl solution at pH 4

Steel type	Treatment	Corrosion rate, µm/yr	Steel type	Treatment	Corrosion rate, µm/yr
4817.........	N	20.1	A387-22......	N	9.7
	I	35.0		I	11.4
	L	19.7		L	17.9
135-mod......	N	13.7	1020.........	N	5.6
	I	6.8		I	18.9
	L	18.7		L	27.9
4130.........	N	11.3	410 SS.......	N	1.5
	I	17.5		I	11.1
	L	12.5		L	17.9

I Ion nitrided. L MLN process. N No treatment.

TABLE 4. – Open-circuit potentials and general corrosion rates of nitrided steels in deaerated 5-wt % NaCl solution at pH 4

Steel type	Treatment	E_{oc}, mV		Corrosion rate, µm/yr	Steel type	Treatment	E_{oc}, mV		Corrosion rate, µm/yr
		24 h	650 h				24 h	650 h	
4817...	I	-695	-711	35.0	135-mod	N	-723	-709	13.7
1020...	L	-774	-728	27.9	4130...	L	-776	-733	12.5
4817...	N	-690	-704	20.1	A387-22	I	-744	-735	11.4
4817...	L	-738	-706	19.7	4130...	N	-728	-719	11.3
1020...	I	-760	-746	18.9	410 SS.	I	-675	-694	11.1
135-mod	L	-628	-739	18.7	A387-22	N	-698	-664	9.7
A387-22	L	-742	-762	17.9	135-mod	I	-707	-667	6.8
410 SS.	L	-661	-740	17.9	1020...	N	-722	-742	5.6
4130...	I	-731	-730	17.5	410 SS.	N	-592	-500	1.5

I Ion nitrided. L MLN processed. N No treatment.

deaerated solution provided by the MLN treatment is inferior to that provided by ion-nitriding or even nontreatment. This conclusion is basically correct, but only for uniform corrosion.

As shown in table 5, both the ion-nitrided coupons and the nontreated coupons were subjected to pitting and exfoliation. For most of the MLN-treated coupons, including the treated 410 SS, it was difficult to visually distinguish the 1-month-immersed and untested coupons; however, the ion-nitrided and nontreated coupons that had undergone the weight-loss testing were easily distinguishable from their untested counterparts because of pitting and exfoliation. The ion-nitrided coupons had pits ranging in depth from 7 to 13 μm following the immersion test. The ion-nitrided steels most subject to pitting were A387-22, 4130, 135-mod, and 410 SS. Ion-nitrided 4817 and 1020 steels underwent coarse uniform corrosion while heavy exfoliation was noted on A387-22 and 135-mod coupons. Nontreated coupons of 4130, A387-22, 135-mod, and 410 steels all underwent pitting with pit depths of a maximum of 13 μm.

ELECTROCHEMICAL TESTS

Open-Circuit Potentials

Table 4 shows the open-circuit (E_{oc}) measured after 24 and 650 h of immersion in deaerated 5-wt % NaCl. The MLN-treated coupons had slightly more negative E_{oc} values as a group and also had the greatest corrosion rates.

Unlike the ion-nitrided and nontreated coupons, initial E_{oc} values for the MLN coupons differed dramatically over the first 24 h of immersion in the test solution. With the exception of the MLN-treated 410 SS, the potentials observed for the MLN-treated steels began to climb from negative to positive potentials greater than +100 mV within the first 30 min of immersion. This phenomenon is shown in figure 4 for the E_{oc} potential over the first 30 h of immersion of the treated and nontreated 135-mod coupons. Note the rapid decline in potential for the MLN-treated coupon after 4 h. This behavior in the E_{oc} is indicative of some type of film formation followed by its dissolution.

TABLE 5. - Corrosion forms observed on weight-loss samples

Steel type	Treatment	Corrosion rate, μm/yr	Corrosion forms observed			Pit depth, μm
			Uniform	Exfoliation	Pitting	
4817..........	N	20.1	X			
	I	35.0	X			
	L	19.7	X			
135-mod.......	N	13.7	X		X	10-13
	I	6.8		X	X	<7
	L	18.7	X			
4130..........	N	11.3	X		X	8
	I	17.5	X		X	<7
	L	12.5	X			
A387-22.......	N	9.7	X		X	10
	I	11.4		X	X	13
	L	17.9	X			
1020..........	N	5.6	X			
	I	18.9	X			
	L	27.9	X			
410 SS........	N	1.5	X		X	<7
	I	11.1			X	<7
	L	17.9	X			

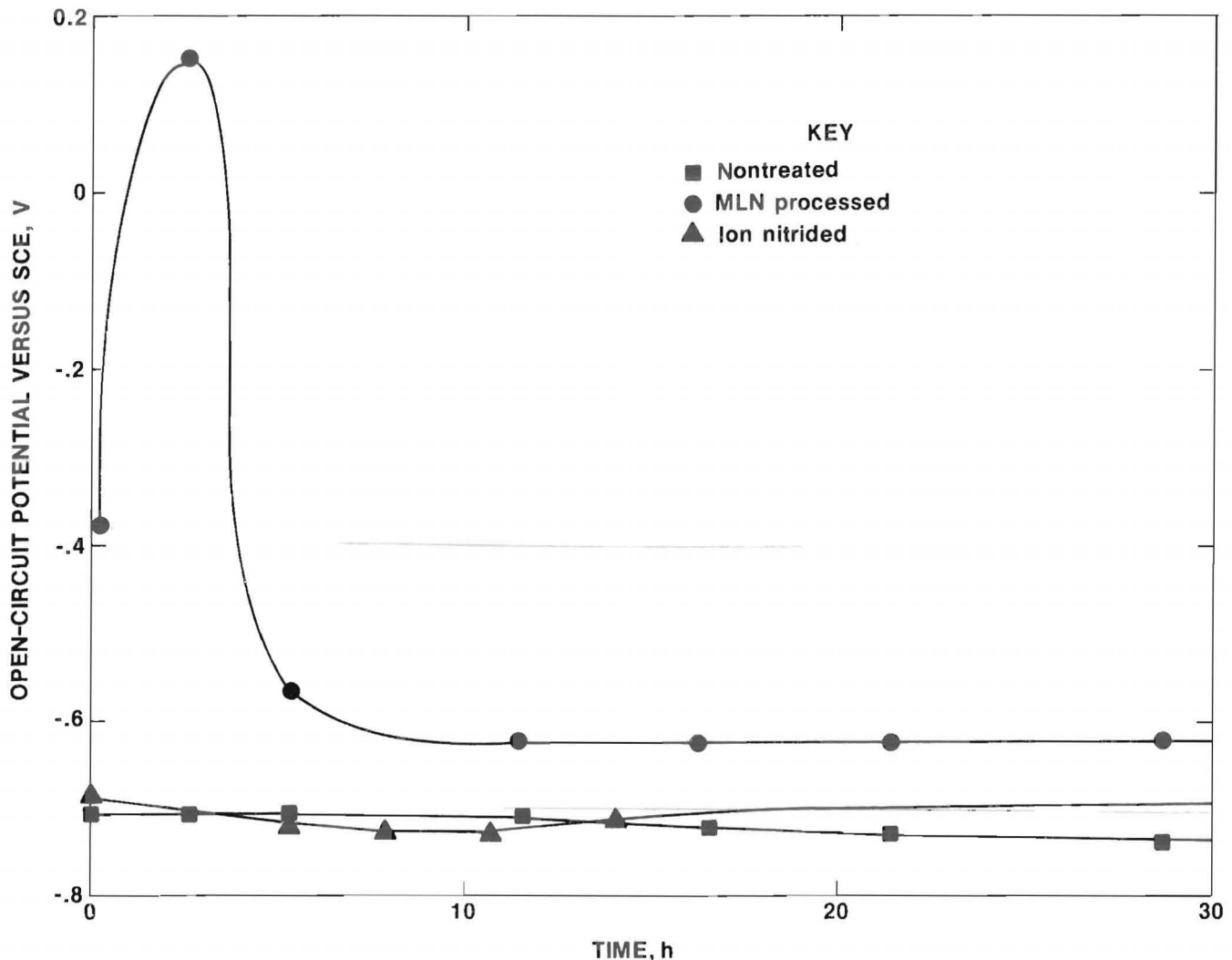I Ion nitrided.   L MLN processed.   N No treatment.

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FIGURE 4. - Open-circuit potential versus time for Nitralloy 135-modified coupons in deaerated 5-wt % NaCl solution at pH 4.

Potentiodynamic Polarization Measurement

Figures 5, 6, and 7 show the results of potentiodynamic polarization tests in de-aerated 5-wt % NaCl for steels A387-22 in the nontreated, ion-nitrided, and MLN-processed condition, respectively. The potentiodynamic polarization responses of the other coupons tested were very similar to those shown in figures 5 through 7. Table 6 shows E_o values along with the observed range of passivation where the current densities were less than 0.4 mA/cm^2. Table 6 also has a comparison of the open-circuit potential, E_{oc} after 650 h, versus the zero current potential, E_o.

The formation of a passive surface film that may result in reduced corrosion can sometimes be detected by comparing the E_{oc} with the E_o. The zero current potential, an experimentally obtained value from potentiodynamic polarization measurements, is the observed potential when the net current is equal to zero (I cathodic = I anodic). During the cathodic portion of a potentiodynamic polarization test, the applied potential polarizes to a potential more negative than the E_o. Because of this cathodic polarization, a reduction of any surface film may result, leaving the surface of the coupon film-free. On the other hand, open-circuit potentials are taken from coupons whose

TABLE 6. – Observed passive ranges,[1] open circuit,[2] and zero current[3] potentials of six nitrided and nontreated steels in 5-wt % NaCl solution at pH 4, deaerated with N_2

Steel type and treatment	Passivation range potentials
	← Negative .... Positive →
	0.8 0.6 0.4 0.2 0.0 0.2 0.4 0.6 0.8 1.0
1020:	
N........	○ ●
L........	●○ ————————————
I........	○● ———————— ————————
L[4]......	●————————————
4817:	
N........	○ ●
L........	●○———————————
I........	○●
4130:	
N........	○ ●
L........	● ○ ————— —————————————————
I........	○ ● ————
135-mod:	
N........	○●
L........	●○ —————————
I........	○● ————
A387-22:	
N........	○●
L........	○ ● —————————————————
I........	○ ●
L[4]......	●———————————————
410 SS:	
N........	● ○
L........	●○ ————
I........	○ ●
	0.8 0.6 0.4 0.2 0.0 0.2 0.4 0.6 0.8 1.0

I Ion nitrided.   L MLN processed.   N No treatment.

[1]Passivation ranges = Horizontal line. Indicated only for current densities stabilized at less than 0.4 mA/cm^2.

[2]Open circuit = ○.

[3]Zero current potential = ●.

[4]Solution aerated with 22% O_2 – 78% Ar.

surfaces have not undergone electrochemical reduction and could have an intact surface film. Passive films will likely shift the open-circuit potential to more positive potentials than the observed E_o value (18); one can distinguish coupons that have formed surface films by comparing their E_o and E_{oc} values.

As shown in table 6, of all the coupons tested in the deaerated 5-wt % NaCl pH 4 solution, only the nontreated 410 SS and the MLN-treated coupons (except for the MLN-treated A387-22) had open-circuit potential values more positive (anodic) than their E_o values, indicating possible surface film formation. Although some reaction shifted the open-circuit potential of the MLN-treated coupons to more positive values in comparison to their E_o values, the shift in potential was not great enough to place the E_{oc} into the passive region where a considerable reduction in the general corrosion would have resulted.
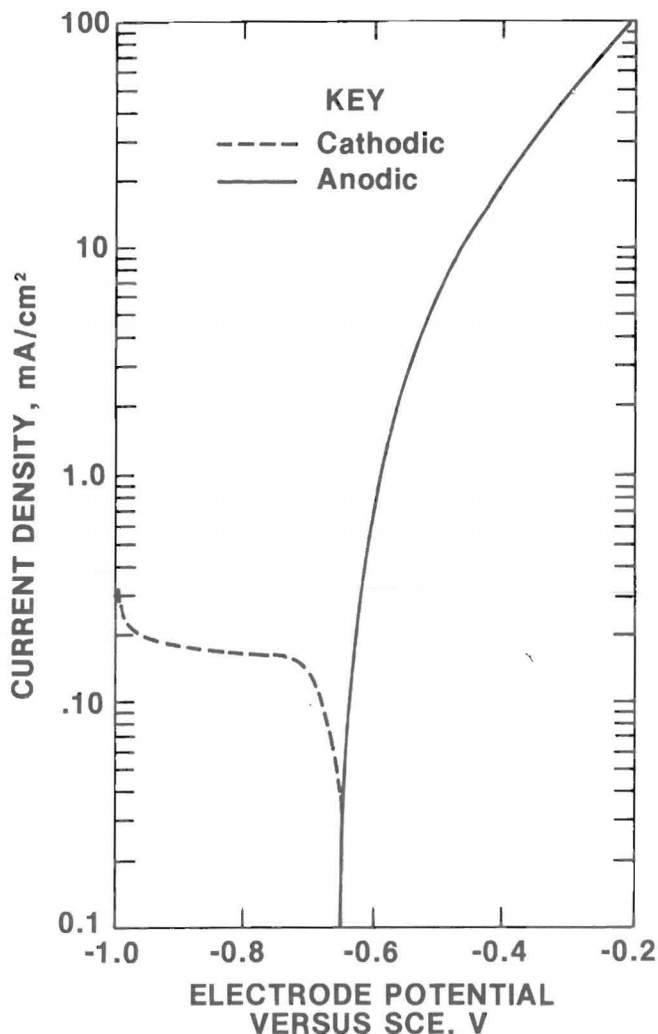
FIGURE 5. - Potentiodynamic polarization curve for type A387-22 steel in 5-wt % NaCl solution at pH 4, deaerated with N_2.

Only the MLN-treated coupons exhibited a passive region (zones of current densities <0.4 mA/cm^2) for all six of the treated steels. Ion-nitrided samples 4817 and A387-22 showed some passivation, but current densities exceeded 0.4 mA/cm^2. The ion-nitrided 410 SS and all the nontreated steels showed no passivity. The passive region for the MLN-treated coupons was generally larger and at lower current density than that observed for the ion-nitrided coupons of the same steel type.

Although these nonpolarized MLN-treated low-alloy and carbon steels have wide passivation region possibilities, they

are not passive at open circuit in N_2 deaerated 5-wt % NaCl. In order for them to have increased corrosion resistance due to the formation of some passive film, their E_{oc} needs to be driven anodically into their passive region. This alteration in the open-circuit potential to a more anodic value can be accomplished by the addition of a passivating agent such as oxygen to the test solution. To test this possibility, the 5-wt % NaCl test solution of pH 4 was aerated with an O_2-Ar mixture (volume ratio 22:78). In this aerated solution, potentiodynamic polarization tests were conducted on MLN-treated 1020 carbon and low-alloy A387-22 steels (fig. 8). Along with exhibiting a passive region of several hundred millivolts, the zero current potential (E_o) in the aerated test solution was shifted from -790 mV to +50 mV for the MLN-treated 1020 carbon steel and from -724 mV to -78 mV for the MLN-treated A387-22 steel. In both cases, E_o was shifted sufficiently that it was within the passive region.

Because of time limitations, only the MLN-treated 1020 and A387-22 coupons were tested in an aerated 5-wt % NaCl solution of pH 4. These two steels represent both low-chromium and nonalloyed steel types. Evaluation of potentiodynamic polarization curves along with open-circuit potentials for the other MLN-treated steels indicate the possibility of their displaying the same behavior as the 1020 and A387-22 in an aerated environment. Unfortunately, time did not allow the testing of the ion-nitrided coupons in an aerated test solution.

It is apparent from the potentiodynamic polarization tests that in an aerated environment the MLN-treated steels readily form a passive film, with passivity exhibited over a large potential range of several hundred millivolts. With the formation of a passive film, a reduction in corrosion rate in an aerated environment should be observed. This reduction in the corrosion rate will be dependent upon the stability and longevity of the surface film formed.
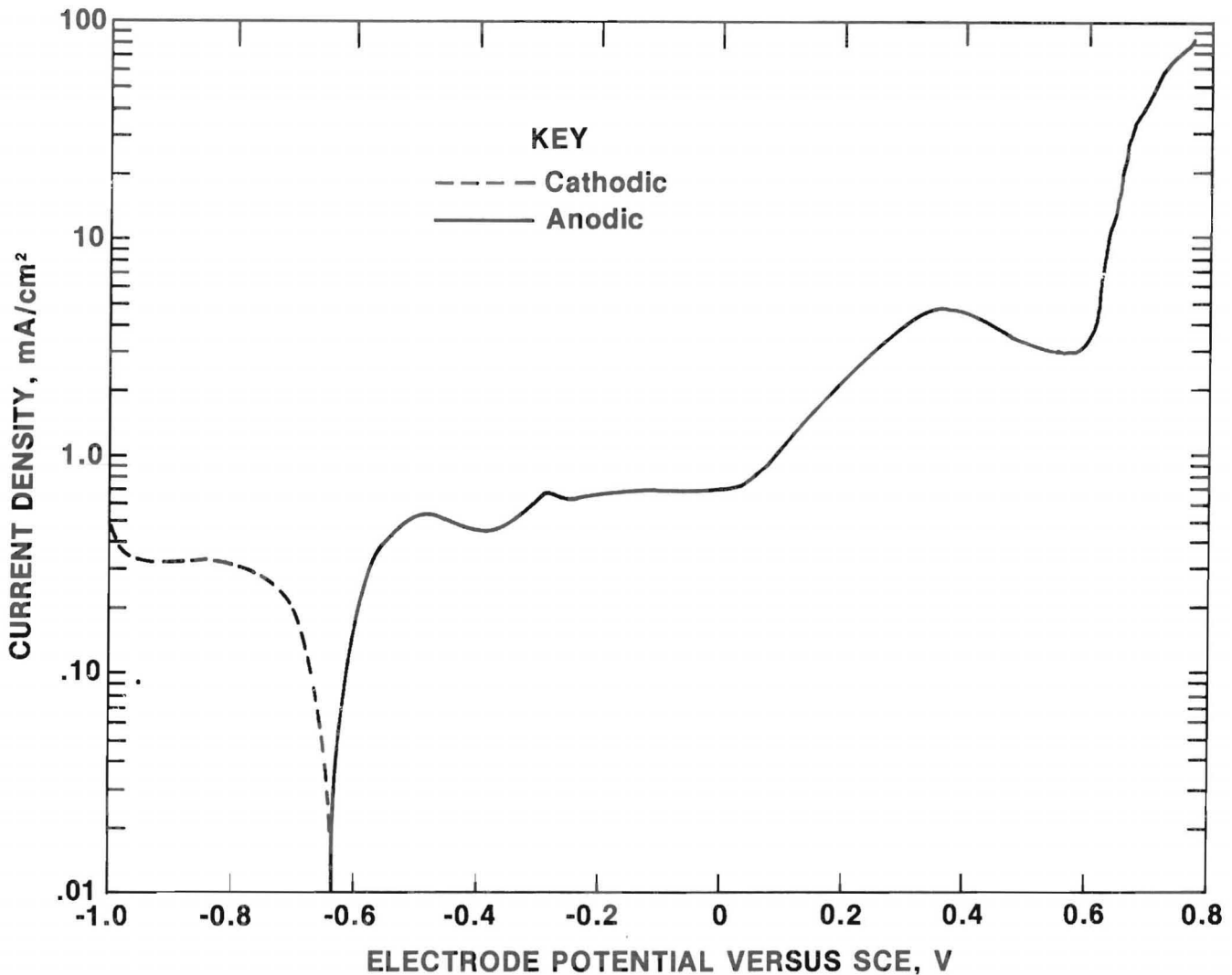
FIGURE 6. — Potentiodynamic polarization curve for ion-nitrided type A387-22 steel in 5-wt % NaCl solution at pH 4, deaerated with N_2.

CONCLUSIONS

Based on the studies presented in this report, the following conclusions can be reached regarding low-alloy and carbon steels in deaerated 5-wt % NaCl at pH 4:

1. With the exception of type 4817 steel (3% nickel), low-alloy and carbon steels treated by the MLN process (a liquid nitriding process followed by oxidizing quench baths) show greater uniform corrosion but reduced pitting compared with nontreated steels.

2. Ion-nitrided, low-alloy, and carbon steels, with the exception of Nitralloy 135-mod, experienced poorer corrosion resistance than did the nontreated steels. The ion-nitrided Nitralloy 135-mod coupons showed a significantly lower corrosion rate than did nontreated steel.

3. Potentiodynamic polarization tests of low-alloy and carbon steels treated using the Melonite QPQ Process (MLN) showed large passive regions. These passive regions were at potentials positive to the open-circuit and zero-current potentials of the sample. Comparing the open-circuit and zero-current potentials, only the MLN-treated samples (except for

the MLN-treated A387-22) and the non-treated 410 SS had open-circuit potentials after 650 h of testing that were positive to corresponding zero-point potentials, indicating possible film formation.
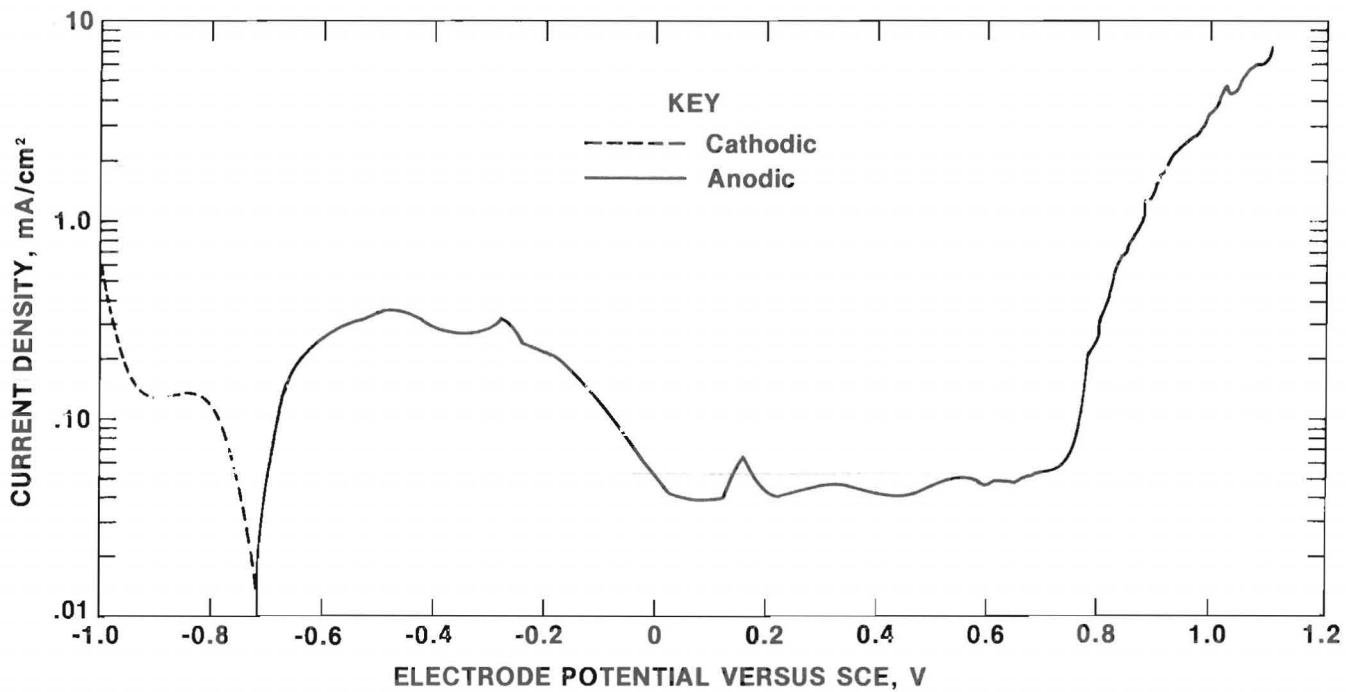

FIGURE 7. - Potentiodynamic polarization curve for MLN-treated type A387-22 steel in 5-wt % NaCl solution at pH 4, deaerated with N$_2$.
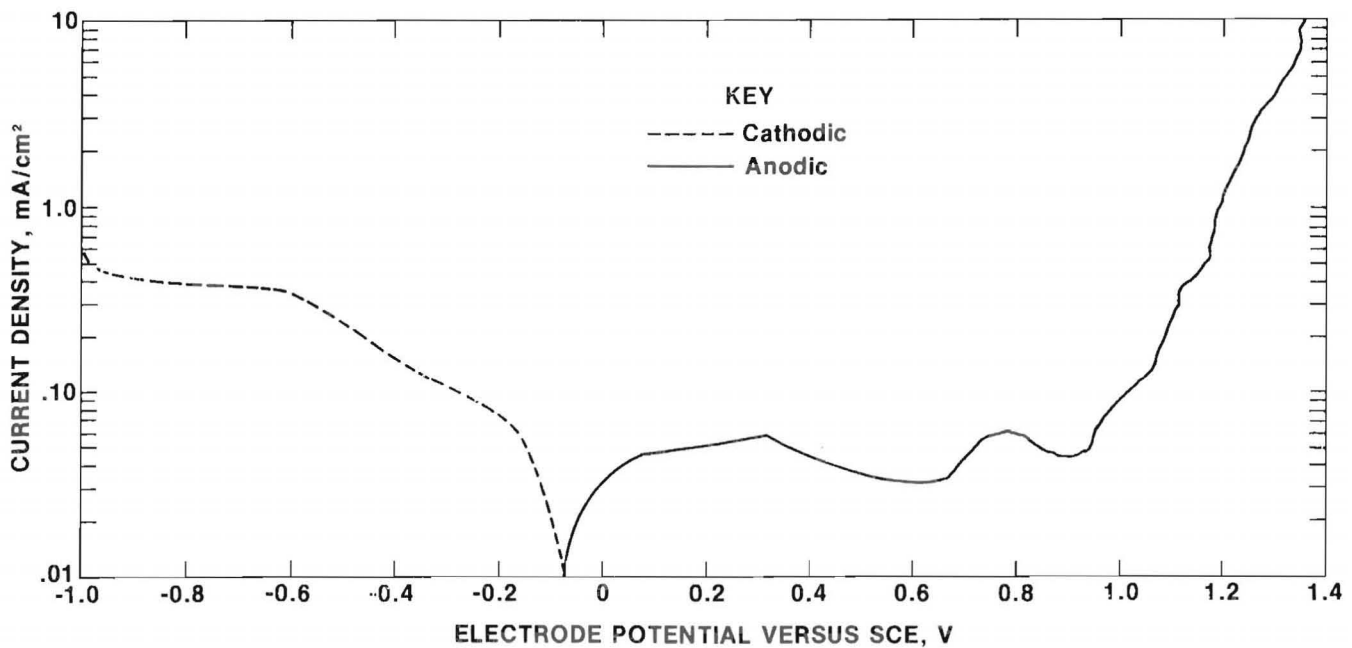

FIGURE 8. - Potentiodynamic polarization curve for MLN-treated type A387-22 steel in aerated 5-wt % NaCl solution at pH 4.

4. Potentiodynamic polarization tests of MLN-treated 1020 and A387-22 steels in aerated 5-wt % NaCl solution at pH 4 indicated an anodic shift of the E_0 of several hundred millivolts. This shift placed the E_0 into the passive region where the reduction in current density indicates superior corrosion resistance of the MLN-treated coupons as compared with their nontreated counterparts.

5. Low-alloy and carbon steels treated by the MLN process and followed by an oxidizing quench bath have the potential for superior corrosion resistance over their nontreated counterparts in aerated chloride environments. To evaluate the extent of this corrosion resistance, further electrochemical testing along with stress and immersion corrosion tests are needed in various aerated solutions.

REFERENCES

1. McQuaid, H. W., and W. J. Ketchum. Some Practical Aspects of the Nitriding Process. Am. Soc. Steel Treat., v. 16, No. 5, 1929, pp. 183-195.

2. Homerberg, V. O., and J. P. Walsted. A Study of the Nitriding Process, Part 1. Ch. in Source Book on Nitriding. ASM, 1977, pp. 56-99.

3. ASM Committee on Nitriding. Gas Nitriding. Ch. in Source Book on Nitriding. ASM, 1977, pp. 107-121.

4. _____. Liquid Nitriding. Ch. in Source Book on Nitriding. ASM, 1977, pp. 122-124.

5. Wood, W. G. Salt Bath Treating as an Alternative for Chromium Plating. Pres. at Workshop Trends in Critical Material Requirements for Steels of the Future Conservation and Substitution Technology for Chromium, (Vanderbilt Univ., Nashville, TN, Oct. 7, 1982), 5 pp.; available from W. G. Wood, Kolene Corp., Detroit, MI.

6. Taylor, A. M., and K. M. Tookey. Ion-Nitriding - A Process With a Future. Metallurg., Feb. 1981, pp. 64-66.

7. Edenhofer, B. Physical and Metallurgical Aspects of Ionitriding. Part 2. Heat Treat. of Metals, No. 2, 1974, pp. 59-67.

8. Klockner, I. G., and J. Conybear. Low Temperature Ionitriding of Precision Parts. 1980, 19 pp.; available from Midland-Ross Corp., Toledo, OH.

9. Mueller, J. Salt Bath Nitriding in Germany. Paper in Proc. Salt Bath Nitriding Seminar (Kolene Corp., Detroit, MI), Oct. 1980, 91 pp.

10. Ohsawa, M. Salt Bath Nitriding of Auto Parts in Japan. Paper in Proc. the Salt Bath Nitriding Seminar (Kolene Corp., Detroit, MI), Oct. 1980. 91 pp.

11. Bil'Chenko, A. V., and V. G. Permyakov. (Corrosion Resistance of Stainless Steel After High-Temperature Nitriding.) Fiz. Khim. Mekh. Mater., v. 6, No. 1, pp. 6-9. 1970; Sov. Mater. Sci. (Engl. Transl.), v. 6, No. 1, 1970, pp. 5-7.

12. Atanasova, I. R., A. V. Bil'Chenko, S. A. Dunaeva, and B. S. Kirchev. (The Effect of Aluminum and Titanium on the Corrosion Resistance of Nitrided Chromium Steels.) Mashinostr., v. 15, 1978, pp. 61-64; Met. Abstr., v. 12, 1979, No. 3541513.

13. Varhoskov, A. E., and I. A. Sedloev. The Effect of Phase Composition on Corrosion Behavior of Ion-Nitriding Layers. Paper in Proceedings, 8th International Congress on Metallic Corrosion 1981 (Sponsored by Int. Cong. Met. Corros., Mainz, West Ger., Sept. 6-11, 1981), v. II, DECHEMA, 1981, pp. 1086-1092.

14. Bidlen, J., and S. Tuleja. (Corrosion Resistance of Nitrided Sheets of Kohal Extra Steel.) Zb. Ved. Pr. Vys. Sk. Tech. Kosiciach (Slov.), Dec. 1972, pp. 107-117; Met. Abstr., v. 7, 1974, No. 350147.

15. Bukarev, V. N., Yu. M. Lakhtin, Ya. Kogan, and V. V. Ponukalin. (The Effect of High Temperature Nitriding on the Corrosion Resistance of Ferrite-Based Steels.) Zashch. Met. (Russian), v. 9, No. 5, Sept.-Oct., 1973, pp. 508-509; Met. Abstr., v. 7, 1974, No. 350387.

16. Hendry, A. The Oxidation Resistance of Nitrided Mild Steel. Corrosion Sci., v. 18, pp. 555-571.

17. Jack, K. H. The Oxidation and Corrosion Resistance of Nitrided Iron Alloys. Eur. Res. Off., U.S. Army, London, Grant DAERO-79-G-0035, 1981, 24 pp.

18. Fontana, M. G., and N. D. Green. Corrosion Engineering. McGraw-Hill, 2d ed., 1978, pp. 319-324.

APPENDIX.--GLOSSARY

Active region.--The potential where an electrode is undergoing sufficient oxidation to result in high current densities and, in turn, a high corrosion rate relative to open-circuit conditions.

Anode.[1]--The electrode of an electrolytic cell at which oxidation is the principal reaction.

Anodic polarization.[1]--The change of the electrode potential in the noble (positive) direction due to current flow.

Cathode.[1]--The electrodes of an electrolytic cell at which reduction is the principal reaction.

Cathodic polarization.[1]--The change of the electrode potential in the active (negative) direction due to current flow.

Compound layer.--A layer up to 50 μm thick consisting of crystals that are commonly formed on steel surfaces undergoing nitriding. These crystals consist mainly of ferric nitrides ($Fe_{2-3}N$, Fe_3N). it is also referred to as the white layer.

Current density.[1]--The current flowing to or from a unit area of an electrode surface.

Diffusion zone (or diffusion layer).--A layer of up to several hundred micrometers found below the white layer or surface of a nitrided metal. Within this layer atomic nitrogen along with nitride compounds can be found.

Exfoliation.[1]--Corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface,

generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance.

Galvanic cell.--Contact of two dissimilar conductors (usually metals).

Open circuit potential (E_{oc}).[1]--The potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from it.

Oxidation.[1]--Loss of electrons by a constituent of a chemical reaction.

Passive.[1]--The state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal.

Pitting.[1]--Corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.

Polarization.[1]--The change from the open-circuit electrode potential as the result of the passage of current.

Potentiodynamic.[1]--The technique for varying the potential of an electrode in a continuous manner at a preset rate.

Reduction.[1]--The gain of electrons by a constituent of a chemical reaction.

Transpassive region.[1]--The region of an anodic polarization curve, noble to and above the passive potential range, in which there is a significant increase in current density (increased metal dissolution) as the potential becomes more positive (noble).

Uniform corrosion (general corrosion).--Corrosion in which there are no distinguishable areas one can denote on the cathode or anode, resulting in equal dissolution rates throughout the surface.

[1]American Society for Testing and Materials. Standard Definitions of Terms Relating to Corrosion and Corrosion Testing. G15-79a in 1980 Annual Book of ASTM Standards: Part 10, Metals--Physical, Mechanical, Corrosion Testing. Philadelphia, PA, 1979, pp. 827-831.

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White layer.—A layer up to 50 μm thick consisting of crystals that are commonly formed on steel surfaces undergoing nitriding. These crystals consist mainly of ferric nitrides ($Fe_{2-3}N$, Fe_4N). Also referred to as the compound layer.

Zero current potential (E_o).—The experimentally observed potential where the net value of the anodic and cathodic current densities is zero.