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CORROSION RESISTANCE OF TRIP STEELS

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Table of Contents

Abstract	v
I. Introduction	1
II. Experimental Procedure	3
A. Materials Preparation	3
B. Electrolyte Preparation	5
C. Mechanical Testing	6
D. Magnetic Testing	7
E. Electrochemical Testing	8
1. Introduction	8
2. Procedure	9
III. Experimental Results and Discussion	12
A. Mechanical Tests	12
B. Electrochemical Testing	14
1. Martensitic Alloys	15
2. Effect of Chloride	20
3. Corrosion Behavior in Artificial Sea-Water	25
4. Effect of Impurities	28
IV. Summary and Conclusions	31
Acknowledgements	33
Appendix	34
References	39
Figures	42

CORROSION RESISTANCE OF TRIP STEELS

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ABSTRACT

The present investigation was undertaken to gain information about the general and pitting corrosion behavior of certain metastable austenitic steels known as TRIP steels, using a potentiodynamic polarization technique.

It was found that partial transformation of austenitic TRIP steels to martensite does not have a significant effect on their corrosion resistance. TRIP steels containing molybdenum show better resistance to pitting attack than widely used commercial stainless steels. For example, in artificial sea-water, a 13Cr-7Ni-4Mo-0.25C TRIP steel has better pitting resistance than type 316 stainless steel.

Finally it was shown that the small amounts of P, S, Si, and Mn that are normally present in commercial steels do not effectively alter the excellent corrosion behavior of TRIP steels.

I. INTRODUCTION

It has been a widely accepted belief that high strength and good ductility in steels cannot be obtained simultaneously. This was based on the assumption that in order to have ductility, large numbers of dislocations must be able to move freely in regions of high stress concentration, whereas high strength could be obtained only if the movement of the dislocations was restricted.¹ In recent years, however, a combination of chemical composition and thermal-mechanical processing has led to a new class of alloys which possess both high strength and good ductility.² These steels have been called TRIP steels (Transformation Induced Plasticity) and are essentially warm-worked austenitic steels that transform to martensite during subsequent straining at service temperature. For example, by a proper thermo-mechanical treatment which includes a 70%-80% prior deformation, TRIP steels having 200,000-300,000 psi yield strength and 50% elongation can be obtained.²

Challande³ and Padilla⁴ have investigated the general corrosion resistance of Cr-Ni-C and Cr-Ni-Mo-C TRIP steels, utilizing an anodic polarization testing procedure. They found that 13Cr-8Ni-3Mo-0.25C and 13Cr-7Ni-4Mo-0.25C TRIP steels have both very good mechanical and very good corrosion-resistant properties. TRIP steels of these compositions show better corrosion resistance than 304 stainless steel and are comparable with 316 stainless steels.⁵

There was no information, however, on the resistance of TRIP steels to localized attack (pitting corrosion), especially in chloride solutions, including sea-water. Nor was there information on the corrosion resistance of TRIP steels that have been cold-worked and thus partly transformed to martensite. Finally, the TRIP steels prepared for previous investigations had been made of high-purity materials, and therefore the effects of the small amount of P, S, Si, and Mn normally present in commercially prepared steels were not known.

The purpose of the present investigation was to obtain information that could be used to clarify these unknown aspects of the corrosion of TRIP steels. The chemical compositions of alloys studied were those recommended by Padilla⁵ as providing excellent mechanical and general corrosion-resistance properties.

II. EXPERIMENTAL PROCEDURE

A. Materials Preparation

Table I lists the compositions of the alloys prepared and also the nominal compositions of the commercial steels used in this investigation.

Alloy A was prepared as a 16-pound ingot by induction melting in an argon atmosphere. The ingot was forged at 1100°C to bars 2 inches wide and 0.8 inch thick which were further reduced to 0.5 inch thickness by cross-rolling at 1100°C. The alloy was then austenized for 90 minutes at 1200°C and ice-brine quenched. After removal of any oxide layer by sandblasting, the alloy was tested with a hand magnet to make sure that it was completely austenized.

The thermomechanical treatment consisted of 80% reduction in thickness by successive rolling at 500°C with heated rolls, the alloy being reheated to 500°C in an electric furnace between passes. The final thickness was 0.1 inch.

Alloy B had been prepared by another researcher.⁵ Except for small differences in their starting and final thicknesses, the method of preparation was the same as described for alloy A; the reduction in thickness was 80%.

Because the impurity contents of alloys A and B (i.e., the concentrations of P, S, Si, and Mn) were appreciably lower than those of commercial steels, an alloy (alloy C in Table I)

Table I. Chemical Composition of Alloys

Alloy	Cr	Ni	Mo	C	Mn	P	S	Si
A	13	7	4	.23	.01	.002	.008	.02
B	13	8	3	.24	.01	.001	.012	.04
C	13	7	4	.21	.96	.006	.025	.18
[†] 4130	.8 - 1.1	-	.15 - .25	.28 - .33	.4 - .6	< .04	< .04	< .20-.35
[†] 304	18 - 20	8 - 10	.5	< .08	< 2	< .04	< .03	< 1.0
[†] 316	16 - 18	10 - 14	2 - 3	< .08	< 2	< .04	< .03	< 1.0

[†] From Metal Handbook Vol. 1 ASM 8th edition (1960)

having chromium, nickel, and molybdenum contents similar to those of alloy A and with impurity levels comparable to those of commercial stainless steels was prepared by adding appropriate amounts of chromium, nickel, molybdenum, and manganese to commercial ASTM 4130 steel; the new alloy was prepared by induction melting in argon, followed by the steps outlined previously.

To obtain TRIP steels with different martensite contents, three pieces were cut from alloy A and each was subjected to different amounts of cold-rolling at room temperature such that their reductions in thickness were 10%, 20%, and 30%. These alloys have been designated as A_{10} , A_{20} , and A_{30} , respectively.

B. Electrolyte Preparation

Three types of solutions were used for the corrosion investigations: (1) 1N sulfuric acid, (2) sodium chloride solutions with various degrees of acidity, and (3) artificial sea-water.

The sulfuric acid solution was prepared by mixing 27.2 ml of 98% H_2SO_4 reagent grade sulfuric acid with doubly distilled water to make 1 liter of 1N acid solution.

The sodium chloride solutions were prepared by first diluting sulfuric acid to four different concentrations and then adding 29.4 g and 14.7 g of anhydrous sodium chloride reagent to one liter of solution to produce 0.5 N and 0.25 N sodium chloride solutions, respectively.

The artificial sea-water was prepared in accordance with the ASTM recommended procedure;⁶ the final composition is listed in Table II.

The starting materials were doubly distilled water and reagent-grade chemicals; the pH of the final solution was adjusted to 8.2 by addition of laboratory standard 0.1 N sodium hydroxide.

Table II.

Chemical composition of artificial
sea water in grams per liter

NaCl	24.53
MgCl ₂	5.20
Na ₂ SO ₄	4.09
CaCl ₂	1.16
KCl	0.695
NaHCO ₃	0.201
KBr	0.101
H ₃ BO ₃	0.027
SrCl ₂	0.025
NaF	0.003

C. Mechanical Testing

One-inch-gage tensile specimens were prepared for each alloy listed in Table I (except the 4130 steel). The dimensions of the specimens are given in Fig. 1. The specimens were tested in air at room temperature on an Instron machine using a crosshead speed of 0.02 cm/min.

Rockwell C hardness measurements were made on unused corrosion samples, prepared as described later. The measurements were made at the centers of the samples to avoid the possible effect of cold work at the edges.

D. Magnetic Testing

The percent of martensite in alloys A, A₁₀, A₂₀ and A₃₀ was determined by the ratio B_s/B_0 where B_s is the saturation induction of the sample and B_0 is a constant which depends on the composition of the alloy.⁷ The saturation induction was measured at room temperature before tensile testing. The apparatus used has been described previously.⁷

Table III gives the amounts of cold work (reduction in thickness) done on alloy A and the corresponding volume percentages of martensite.

Table III.

Martensite Content of Cold-Worked Alloys		
Alloy	Reduction in Thickness, percent	Vol percent Martensite
A	0	0*
A ₁₀	10	7
A ₂₀	20	20
A ₃₀	30	30
* not detectable		

De Miramon⁷ has observed that for measurements such as those made in this investigation, the precision of the instrument is such that it can detect magnetic volumes of 0.1% or even less.

E. Electrochemical Testing

1. Introduction

The corrosion characteristics of the alloys were evaluated by the potentiodynamic polarization method. Since the introduction of this method by Edeleanu in 1954⁸ there have been numerous articles on the theoretical and experimental aspects of this technique, and today it is a widely accepted and used tool in modern corrosion research.

A typical polarization curve for a passivating metal is presented in Fig. 2. The important parameters are:

E_0 = Open circuit potential; the potential between the sample and the counter electrode when no external current is applied.

I_{Cr} = Critical current density; the maximum corrosion current or current necessary to passivate the metal.

I_p = Current density in passive region.

E_p = Passivation potential; potential at which metal becomes passive.

E_T = Transpassivation potential; potential at which metal loses its passivity.

E_B = Breakdown potential; potential at which (in the presence of chloride ion) pitting starts.

Details on the importance of each parameter are available in the books by Uhlig⁹ and Greene.¹⁰ Also any modern corrosion text has a chapter on the validity and the basic theory of the polarization method.^{9,11} The concept of breakdown potential, however, is relatively new, and a rather comprehensive explanation of this parameter is given in the appendix.

2. Procedure

Square pieces approximately 1.5 cm^2 in area were cut from each alloy and were ground to circular disks having diameters of approximately 1.2 cm. Each sample was mounted in self-curing resin, and surface scratches were removed by polishing with silicon carbide papers 240 through 600 grit sizes. The final polishing was done with the help of 1 μ diamond paste on a canvas wheel. The resin was then dissolved in methyl-ethyl-ketone (MKE), and the polished sample was thoroughly washed twice in ethyl alcohol and then in doubly distilled water and dried.

The polarization cell used was the one recommended by ASTM.¹² A schematic diagram of the cell is shown in Fig. 3. A 1-liter round-bottom flask had been modified by the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes, and a thermometer. The probe salt bridge separated the bulk solution from the saturated calomel reference electrode, and the probe tip could be easily adjusted to bring it close to the working electrode. A detailed description of the cell and its components has been given by Greene.¹⁰ The specimen holder used for this investigation was similar to the one

suggested by Mayers.¹³ A schematic diagram of the holder is given in Fig. 4. The material used for fabrication were polycarbonate and teflon. The electrode assembly exposed only polycarbonate and the specimen to the electrolyte. A 3/8-inch-diameter copper rod, which was in contact with the back face of the specimen, supplied the electrical continuity through the system. A teflon gasket compressed against the specimen by the polycarbonate cover provided a virtually crevice-free, leakproof seal and controlled the exposed surface area. The inside diameter of the gasket, 0.445 inch, was selected to expose a surface area of 1 cm^2 so that the measured current was also the current density.

A schematic diagram of the entire system is given in Fig. 5. The apparatus set-up was almost identical to one suggested by France.¹⁴ Exceptions were the use of a motor to scan the potential instead of an automatic programmer, and the use of a low-pass R.C. filter with a time constant of 1.5 second to cut down the internal electrical noise of the system. Also, for some experiments, the polarization cell was enclosed inside a grounded copper shield to decrease the external noise.

Except for the experiments conducted in artificial sea water, all solutions were purged for a minimum of one-half hour with oxygen-free hydrogen gas at the rate of $150 \text{ cm}^3/\text{min}$ prior to immersion of the test specimens. Data recording was started one-half hour after the immersion of the specimen, hydrogen being introduced at a somewhat lower rate during the measurements. For experiments conducted in artificial sea-water, no hydrogen was introduced to the solution before

or during the measurements; also, due to the instability of the open-circuit potential in artificial sea water, recording was started two hours after the immersion of the sample.

The scanning rate used for all experiments was 1.4 volts/hr. All experiments were started within 10 mV of open-circuit potential,¹² and the voltage was scanned toward the noble direction. Experiments were stopped just beyond the transpassivation potential (E_T) in the case of sulfuric acid solutions or just beyond the breakdown potential (E_B) in the case of chloride solutions.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Mechanical Tests

The results of mechanical testing for all the alloys used in this investigation are given in Table IV. The values reported for types 304 and 316 stainless steels are taken from the literature.

Alloys A through C shows much higher yield and ultimate strength than types 304 and 316 stainless steels. Also, the percent elongation for alloys A through C indicate that these alloys have good ductility.

Alloy C which has higher impurity content and slightly lower carbon content than alloy A shows a somewhat higher yield strength and lower tensile strength than alloy A.

There have been extensive investigations on the excellent mechanical properties of TRIP steels.^{15,16,17} The mechanism and the principles involved also have been thoroughly presented.^{2,18}

Table IV. Mechanical Properties

Alloy	Yield Strength, Ksi	Tensile Strength, Ksi	Elongation, pct	Rcd. in area, pct	Hardness
A	170	251	30	43	R _C 48
A ₁₀	178	259	25	42	R _C 49
A ₂₀	210	262	25	42	R _C 52
A ₃₀	249	269	24	40	R _C 55
B	187	231	38	38	R _C 45
C	194	245	32	39	R _C 51
304 (a)	35	85	55 [b]	65	R _b 80
316 (a)	35	85	55 [b]	70	R _b 80

(a) From "Metal Handbook" Vol. 1 ASM (1961)

(b) 2 inch gage length

B. Electrochemical Testing

In order to check the experimental technique and instrumentation, polarization curves of three alloys were determined and compared with the curves reported by previous investigators. The alloys chosen were commercially available stainless steels 304 and 316 and alloy B. The electrolyte used for the commercial steels was 1N sulfuric acid. To facilitate the comparison with previous work,⁵ the solution used for alloy B was 2N sulfuric acid. The polarization curves are given in Figs. 6, 7, and 8. A comparison of the values of I_{Cr} , I_p and E_p found for these alloys with previously reported values is given in Table V.

Table V.

Anodic Polarization Results for
Alloy B and Stainless Steels 304 and 316

Alloy	Source	E_p Volts vs. SCE	I_{Cr} μ amp/cm ²	I_p μ amp/cm ²
S.S. 304	Present Investigation	-.24	72	8
"	Padilla (5)	-.22	84	4
"	France & Lietz (14)	-.30	35	7
S.S. 316	Present Investigation	-.20	12	4
"	Fontana & Greene (11)	-.18	15	2
"	Wilde & Greene (19)	-.22	9	-
B	Present Investigation	-.24	17	7
	Padilla (5)	-.25	15	8

The values obtained for alloy B are in close agreement with the values obtained previously.⁵ The commercial alloys show small differences in the values; such differences, however, are not unusual and are due partly to variations in experimental procedure (scanning rate, etc.) and partly to variations in composition.

1. Martensitic Alloys

Polarization curves for the partly martensitic alloys showed only slight variations from one another, so to determine whether corrosion properties depend on martensite content, several tests were made on each of the alloys A, A₁₀, A₂₀, and A₃₀. The polarization curves are given in Figs. 9 and 12. Tables VI, VII, VIII, and IX give the anodic polarization results for each run and the average values for the 0%, 7%, 20%, and 30% martensitic alloys, respectively.

Table VI.

Polarization Results for Alloy A
(0 vol% Martensite)

Run	E _O Volts vs. SCE	E _P Volts vs. SCE	I _{Cr} μ amp/cm ²	I _P μ amp/cm ²
1	-.24	-.22	5.9	3.4
2	-.23	-.22	6.2	3.3
3	-.25	-.22	6.1	3.2
Avrg	-.24	-.22	6.1	3.3

Table VII.

Polarization Results for 7 vol%
Martensitic Alloy

Run	E_O Volts vs. SCE	E_P Volts vs. SCE	I_{Cr} $\mu \text{ amp/cm}^2$	I_P $\mu \text{ amp/cm}^2$
1	-.25	-.20	5	3
2	-.23	-.18	6	3
3	-.27	-.20	5.5	3
4	-.26	-.21	8	3.5
Avrg	-.25	-.20	6.2	3.1

Table VIII.

Polarization Results for 20 vol%
Martensitic Alloy

Run	E_O Volts vs. SCE	E_P Volts vs. SCE	I_{Cr} $\mu \text{ amp/cm}^2$	I_P $\mu \text{ amp/cm}^2$
1	-.26	-.21	7.5	3.5
2	-.28	-.23	10	4.5
3	-.28	-.24	8	4.5
4	-.29	-.25	9	4.5
Avrg	-.28	-.24	8.6	4.3

Table IX.

Polarization Results for 30 vol%
Martensitic Alloy

Run	E_O Volts vs. SCE	E_P Volts vs. SCE	I_{Cr} $\mu \text{ amp/cm}^2$	I_P $\mu \text{ amp/cm}^2$
1	-.29	-.25	11.5	3.5
2	-.31	-.27	11.5	4
3	-.30	-.25	11.5	4.5
4	-.29	-.25	11	5
Avrg	-.30	-.26	11.4	4.3

The results for the individual runs agree reasonably well, the differences probably being due to variations in local stresses caused by machining and/or imperfections on some polished surfaces. A comparison of the average values for E_0 , E_p , I_{Cr} , and I_p is given in Table X.

Table X.

Comparison of Average Results For Martensitic Alloys

Alloy	% Martensite	E_0 Volts vs. SCE	E_p Volts vs. SCE	I_{Cr} (μ amp/cm ²)	I_p (μ amp/cm ²)
A	0	-.23	-.22	6.1	3.1
A ₁₀	7	-.25	-.20	6.2	3.1
A ₂₀	20	-.28	-.24	8.6	4.3
A ₃₀	30	-.30	-.26	11.4	4.3

The corrosion characteristics of martensitic alloys, unlike austenitic alloys, are not fully known. Some corrosion literature has reported that martensitic alloys possess poor corrosion properties. Fontana¹¹ has stated that martensitic steels are less resistant to general corrosion than ferritic or austenitic steels. Fink²⁸ has concluded that martensitic alloys are susceptible to pitting in seawater.

Based on such reports, it was feared that the existence of a martensitic phase in TRIP steels might have a deleterious effect on

their corrosion properties. Table IX shows that although the corrosion current tends to increase with increasing martensite content, the magnitude of the increase, which may be of interest for scientific reasons, is relatively unimportant from an engineering point of view. Both alloy A with 0% martensite and alloy A₃₀ with 30% martensite will readily passivate in aerated solutions (alloys having I_{Cr} of less than 100 amp/cm² will immediately passivate upon immersion in aerated solutions¹¹).

The fact that the increase in corrosion current density is so slight may be due to the effect of molybdenum. Evans²⁰ has suggested that molybdenum oxide covers the main protective layer (mainly Cr₂O₃ for stainless steel) and prevents or delays the breakdown of passivity. The exact nature of molybdenum film (thickness, growth rate, stability) is not known, and, as Evans points out, a detailed investigation of protective films containing molybdenum is long overdue.

Another trend is the effect of the martensite content on the open-circuit (E_O) and passivation (E_p) potentials - the higher the martensite content the more negative E_C and E_p become. In other words, an alloy containing martensite passivates slightly more readily than an alloy of the same chemical composition without martensite. Uhlig⁹ has suggested that if two steels, having corrosion potentials E_A and E_B , respectively, are coupled, the couple will corrode at a potential E_C which has a value between E_A and E_B , and its precise value will depend on the relative areas of the two steels. The lowering of the open and passivation potentials in partly martensitic alloys is, then, probably

due to local galvanic coupling between the martensite and austenite phases. Generally, martensitic alloys have much lower E_0 and E_p values than austenitic alloys.²⁸ Based on Uhlig's argument, it is reasonable to expect E_0 and E_p to move towards more negative values as the content of martensite increases.

Finally it should be reemphasized that the changes in corrosion rate due to martensite are relatively unimportant, and a typical TRIP steel such as alloy A retains its excellent corrosion resistance regardless of the phase changes caused by cold working.

2. Effect of Chloride

To investigate the pitting-corrosion characteristics of a TRIP steel, potentiodynamic polarization tests were made on alloy A in 0.25N and 0.5N sodium chloride solutions of various acidities. The polarization curves are given in Fig. 13 through 18, and the results are summarized in Table XI.

As can be seen from Figs. 13 to 15, no breakdown occurred in 0.25N sodium chloride solutions, even with sulfuric acid concentrations as high as 2 normal. On the other hand, breakdown was observed for 0.5N sodium chloride solutions at sulfuric acid concentrations as low as 0.1N.

From these results the following trends can be observed. (1) A minimum chloride concentration is necessary in order to have pitting breakdown. (2) In solutions having or exceeding the minimum chloride concentration, the breakdown potential depends on the pH of the solution - the lower the pH the lower the breakdown potential.

Table XI.

Polarization Results for Alloy B in Media Containing Chloride

NaCl Conc. in Normal	H ₂ SO ₄ Conc. in Normal	E _O Volts vs. SCE	E _P Volts vs. SCE	I _{Cr} (μ amp/cm ²)	I _P (μ amp/cm ²)	E _B Volts vs. SCE
0.25	0.5	- 0.32	- 0.27	43	4	*
	1.0	- 0.35	- 0.26	280	4	*
	2.0	- 0.32	- 0.26	450	4	*
0.5	0.1	- 0.41	- 0.37	35	4	+ 0.66
	0.5	- 0.40	- 0.36	190	4	+ 0.41
	1.0	- 0.41	- 0.37	700	4	+ 0.38

*
no breakdown

(3) The critical current density, I_{Cr} , is sensitive to both chloride concentration and acidity: the higher the chloride and/or acidity the higher I_{Cr} becomes. (4) The current density in the passive stage, I_p , remains virtually constant regardless of the acid or salt concentration.

In environments containing appreciable concentrations of chloride or bromide, in which they otherwise remain essentially passive, all stainless steels tend to corrode at localized areas and to form deep pits.⁹ A summary of present-day theories of pit formation and different methods of investigation of pitting characteristics of metals and alloys is presented in the appendix.

Based on the trends observed in this investigation the following comments can be made in regard to the effect of chloride:

a) As observed in this investigation and emphasized by Kolotyркин,²¹ aggressive anions can stimulate the development of pitting corrosion only if they are present in the solution in greater than certain critical concentration. This phenomenon can be explained in terms of competitive adsorption of chloride ion with oxygen of the passive film.²¹ The metal has typically greater affinity for oxygen than for chloride ion, but when the original solution has a high chloride content and the potential is made more noble, the concentration of chloride ions at the metal surface increases, eventually reaching the critical value that allows chloride to displace adsorbed oxygen in the passivating film.⁹

The critical concentration of the aggressive anion depends on the nature of the metal or alloy.²¹ Stolica²² has presented an extensive report on the critical concentration for different types of Fe-Cr alloys. He reports that pure iron will develop pits in solutions containing a chloride concentration as low as 0.0003N. Introduction of

chromium enhances the pitting resistance. A 20Cr-Fe alloy shows a critical concentration of 0.1N. Interestingly enough, introduction of as much as 10% of nickel does not increase the critical concentration. The critical concentration for alloy B is between 0.25N and 0.5N (see Table XI). The only commercial alloys that show critical concentrations as high or higher are alloys containing 25% or more chromium.²² The high critical concentration for alloy B can be partly attributed to the contribution of molybdenum, which enhances the pitting resistance,²³ and to a contribution from the special thermomechanical treatment of TRIP steels. The exact nature of this contribution is not known.

b) There has been little work concerning the influence of the pH on the breakdown potential.²⁴ Leckie and Uhlig²⁵ have made a series of experiments on commercial 18-8 stainless steels in 0.1N NaCl solutions in the pH range of 2 to 12, and have concluded that breakdown potential is not appreciably affected by the pH of the solution in this range. The results obtained in this investigation have shown, however, that in much more acidic solutions containing 0.5N NaCl, E_B varies from +380 mv to +660 mv, depending on the pH of the solution. Smialowska²⁴ in his recent review of pitting literature cites reports that contradict the conclusion of Leckie and Uhlig. A possible reason for this discrepancy is the fact that Leckie and Uhlig's experiments were conducted at pH values greater than 2 and therefore their conclusion should not be applied to the entire range of pH. The pH of the solutions used in this investigation was considerable less than 2.

c) The increase of critical current due to the increase in acidity is a well established fact and is reported in standard corrosion texts.^{9,11} It is attributed to the increase in oxide solubility with increase of acidity of the solution, and therefore, difficulty in forming protective oxide layer at the corroding surface.²⁰

d) The effect of chloride on the critical current density, on the other hand, is not well understood. Trautenberg²⁶ has suggested the formation of Cl-Fe complexes, which simply carry Fe^{+++} away from the surface, preventing the rapid formation of a protective Fe_2O_3 layer and therefore increasing the critical current. Ambrose and Kruger,²⁷ on the other hand, by the use of ellipsometry have concluded that the kinetics of film growth is completely different in the presence of chloride ions than in the absence of those ions. The growth in the presence of chloride ion is continuous.²⁷

e) In regard to the fact that I_p is independent of hydrogen ion content of the solution, it can be argued that the low corrosion current in the passivated state is due to the diffusion of Fe^{+++} ions through defects of the protective film, the number of such defects being a property of the oxide film and not of the electrolyte.

From the engineering point of view the following conclusions can be drawn:

Alloy A, a typical TRIP steel, will not spontaneously passivate in an unstirred solution containing a high chloride concentration at a low pH. However if an external (cathodic) potential is applied, or in some cases, if the solution is stirred the alloy will passivate and

then show excellent resistance to general corrosion. (Stirring enhances oxygen transport to the surface of the corroding metal, and thus may cause passivation). Alloy A shows better resistance to pitting than commercial steels that have chromium content as high as 25%.

3. Corrosion Behavior in Artificial Sea-Water

Potentiodynamic polarization curves obtained when artificial sea-water was used as electrolyte are given in Figs. 19 and 20.

Figure 19 shows that alloy B has a moderately higher breakdown potential than a commercial 316 stainless steel, thus a higher resistance to pitting.

Figure 20 shows a large difference in breakdown potential between alloy A and 316 stainless steel. Alloy A has a much higher E_B and therefore is a far better material with respect to resistance to pitting attack. Interestingly enough, alloy A₂₀, which has the same chemical composition as alloy A but is partly martensitic, shows an even higher breakdown potential.

To check the consistency of the breakdown potential measurements, two separate tests were made on each alloy, each time using a newly polished sample and a fresh electrolyte solution. The results are summarized in Table XI.

Table XII.

Breakdown Potentials in Sea-Water

Test	Alloy	E _b (volts)
1*	S.S. 316	+ 0.29
2a*	B	+ 0.42
2b	B	+ 0.40
3a*	A	+ 0.65
3b	A	+ 0.64
4a	A ₂₀	+ 0.84
4b*	A ₂₀	+ 0.85
* Polarization curves of these tests are presented in Figs. 19 and 20.		

As can be seen, the breakdown potential is quite reproducible.

Fontana and Green,¹¹ in their listing of materials that show the least general corrosion in sea water, have placed the austenitic 316 stainless steel after hastelloy C and titanium as the third best material in the series. According to them type 316 in actual long-range exposure shows less than 0.1 mil per year corrosion rate. Such a corrosion rate is considered excellent, and therefore one might expect that type 316 should be a suitable material for marine environment. This is not the case, because it is subject to pitting corrosion. Pit initiation in type 316 is slow, but when pitting starts, penetration is as fast as in type 304.²⁸

Hastelloy C and titanium are immune to both general and pitting attack, and they even withstand crevice corrosion and therefore technically are ideal materials for sea water. The problem with these alloys, and also with alloys of high nickel content such as Monel, is that their basic price plus the labor cost for shaping, cutting, welding and installation is so high that it prevents their use for common wide-scale applications. Therefore, there is still a critical shortage of materials that, on the one hand, can withstand all types of attack in a marine environment and, on the other hand, are economically reasonable.

The results obtained here show that some compositions of TRIP steels might be an answer to the problem.

First of all, as seen in Figs. 19, and 20, the alloys tested in sea-water, namely alloy A, alloy A₂₀, alloy B, and type 316, have critical current densities less than $100 \mu\text{amp}/\text{cm}^2$, so all of them will passivate in aerated sea-water and then (from their low passive current densities) show a very small general corrosion rate. Pitting susceptibility, therefore is the correct criterion for their comparison.

Alloy B, which has lower chromium and nickel contents and the same molybdenum content as type 316 stainless steel, shows better pitting resistance than type 316. This can only be attributed to its unique thermomechanical treatment, but the reason for the effect is not known.

Increase of the molybdenum content from 3% to 4% (alloy A) further improves the pitting resistance. This is not unexpected; the beneficial effect of molybdenum has been widely reported in recent literature.⁹ The unexpected phenomenon is that Alloy A, when partly transformed to martensite by cold working (alloy A₂₀), shows the best pitting characteristics of them all. The breakdown potential is so high that the cold-worked alloy is almost immune to pitting in the potential range of stability of water.* There is no sound theory, as of today, that can explain the positive contribution of the martensite phase on breakdown potential.

Based on the results obtained in this section the following conclusion can be drawn: A 13Cr-8Ni-3Mo-0.25C TRIP steel has a better pitting resistance than type 316 stainless steel. An increase in molybdenum content and/or the presence of martensite further improves the pitting characteristics of TRIP steels in sea-water.

4. Effect of Impurities

As mentioned previously, a special alloy (alloy C) was prepared having chromium, nickel, molybdenum, and carbon contents comparable to those of alloy A and also having the small amounts of impurities (Mn, P, S, Si, etc.) that usually exist in most commercial alloys. The potentiodynamic curve obtained for this alloy is given in Fig. 21.

The curve does not show a sharp critical current maximum. This phenomenon is not uncommon for steels containing molybdenum.⁹ The maximum corrosion current density is about $12 \mu \text{ amp/cm}^2$ and the minimum about $5 \mu \text{ amp/cm}^2$.

* Water is stable up to around 1.23 volts.

Comparing the general shape of the polarization curves of alloy A (Fig. 9) and alloy C, there is little or no significant difference.

Sauby,²⁹ influenced by an article by Armijo,³⁰ has expressed fear that if the impurity level of a TRIP steel reaches that of commercial steels, there will be major deterioration in its general corrosion resistance. Wilde and Green³¹ also have reported that major changes would occur in the critical anodic current density (I_{Cr}) of a 304 stainless steel if the concentration of certain impurities, such as sulfur or phosphorus, were to be changed by a small amount. They even have developed an empirical equation relating the impurity content of this alloy to its critical current density.

The results obtained in the present investigation have shown, on the other hand, that the corrosion resistance of a well balanced TRIP steel does not become significantly altered by the normal small levels of impurities.

The following can be offered as reasons for the discrepancies:

(a) The method used by Armijo³⁰ was developed for testing intergranular corrosion, and is not applicable to the general corrosion rate. The impurities singled out by Armijo³⁰ as the major elements initiating intergranular corrosion do not necessarily increase the general corrosion rate as feared by Sauby.²⁹

(b) In regard to intergranular corrosion, it seems that Armijo's conclusion should not be taken as a valid rule for all types of austenitic steels. His conclusions are based on a rather limited survey which excludes many types of austenitic steels, especially those containing molybdenum. There are strong indications, for example,

that molybdenum counteracts the negative effect of phosphorus by forming phosphorus molybdate which even facilitates passivation.³² There are also indications that copper, if present as an impurity, counteracts the effect of sulfur,³² which is mentioned as one of the most undesirable elements in regard to intergranular and general corrosion.³⁰

Uhlig⁹ recently has suggested that intergranular attack due to phosphorus and sulfur might occur in the transpassive region. Such attack if it exists should not be a matter of much concern because in actual practice there are very few corrosive solutions that have such high oxidizing potential as to force the alloy to transpassive region.

(c) In regard to the empirical equation developed by Greene and Wilde,^{31,33} which predicts high increases in the I_{Cr} value due to impurities, it should be mentioned that even according to them the equation does not work for all types of steels. Generally, it seems that the equation is valid only for type 304. For instance, if the equation is used for type 316 stainless steel it gives corrosion rates that differ grossly from the experimental values.

To summarize, it seems that the effect of small concentrations of impurities on corrosion depends on the major alloying elements and on their possible reactions with the impurities. Sometimes the effect of one impurity counteracts the effect of another so that the addition of the two elements causes no major change in corrosion. In the case of a well balanced TRIP steel, such as alloy C, the impurities usually present have no significant effect on its corrosion resistance.

IV. SUMMARY AND CONCLUSIONS

An investigation was conducted on the general and pitting corrosion properties of TRIP steels having compositions of 13Cr-8Ni-3Mo-0.25C and 13Cr-7Ni-4Mo-0.25C using a potentiodynamic polarization technique. These alloys had shown excellent mechanical properties. The conclusions obtained are as follows:

1. Partial transformation of these metastable austenitic TRIP steels to martensite by cold work does not have any significant effect on their corrosion resistance. The partly martensitic TRIP steels, like the austenitic TRIP steels, passivate readily in aerated solutions and show excellent resistance to general corrosion.

2. In moderately acidic solutions (pH greater than 1) and in the presence of chloride ions, the TRIP steels passivate readily. In highly acidic solutions (pH less than 1) containing chloride ions, they do not passivate spontaneously, but if passivated (by an external potential, for example) they will show excellent resistance to general corrosion. The TRIP steels show better resistance to pitting corrosion than commercial steels that have chromium contents as high as 25%.

3. The austenitic TRIP steels tested show excellent resistance to both general and pitting corrosion in sea-water. When partly transformed to martensite, they show even better resistance to pitting.

The results obtained in this investigation indicate that TRIP steels of the compositions investigated may be suitable materials for marine applications, and, from a corrosion point of view, are a very attractive alternative to the widely used types 304 and 316 stainless steels.

The effects of normal impurities on the corrosion behavior of the TRIP steels are insignificant. An alloy having the same chemical composition as a high-purity TRIP steel tested, but with impurity levels comparable to those of commercial alloy steels, showed excellent resistance to general corrosion.

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APPENDIX

Pitting Corrosion

Among all the specific types of corrosion, pitting holds a special place because it is one of the most dangerous and common types of destruction of metals in aqueous electrolyte solutions.

Although there have been many attempts to present a general theory that can explain every aspect of pitting phenomena, none of the theories presented has so far been universally accepted. Based on two comprehensive review articles on pitting,^{21,24} the following theories are the ones that are most discussed.

Hoar,³⁴ as early as 1949, suggested that formation of pits is due to increase of acidity of the solution at the active sections, as a result of which metal passes into the solution in the form of soluble salt instead of being precipitated as oxide.

Another theory, suggested by Kolotyrtkin,²¹ is that the formation of pits is connected with the adsorption displacement of passivating oxygen, at the surface of the metal, by the aggressive anion. Uhlig and coworkers have also advocated such a theory.²⁵

The most recent theory, presented in Smialowska's review paper,²⁴ is that pit initiation is due to the adsorption of aggressive anions on the surface of the oxide film, followed by the penetration of ions through the film. This theory, which is known as "adsorption without displacement," is partly based on Hoar's recent article,³⁵ in which he has suggested that anion entry, without exchange in the film, produces a greatly induced ion conduction in the "contaminated" oxide

film, which thus becomes able to sustain high current density and to produce pitting.

Experimentally, it has been observed that if anodic polarization tests are conducted on certain alloys in solutions containing chloride, and the potential is scanned from open circuit potential (E_0) toward the noble direction, there is a potential known as the breakdown potential (E_B) at which the corrosion current suddenly shows an enormous increase. If scanning is continued beyond this potential, pits develop on the surface. In the potential range E less positive than E_B no pitting occurs.

The breakdown potential phenomenon has been interpreted in previous theories in the following manner.

According to the Uhlig-Kolotyrkin "adsorption-displacement" theory, the corroding metal has typically a greater affinity for oxygen than for Cl^- , but as the potential is made more noble the concentration of Cl^- ions at the surface increases and eventually (at E_B) the concentration of Cl^- reaches a value that allows Cl^- to displace oxygen.

Hoar, in the "adsorption without displacement" theory, explains the breakdown potential as that value needed to build up an electrostatic field within the passive film sufficient to induce Cl^- penetration to the metal surface.³⁵

The more positive the E_B , the more resistant the metal is to pitting attack.

The deleterious effect of chloride on anodic passivation of Al, Fe, Cr, and Fe-Cr alloys has not been observed for all metals. Ti, Ta, Mo, W, and Zr do not lose their passivity on anodization in solutions containing chloride.

Vijh³⁶ recently has suggested a mechanism for pitting, which tries to explain why some metals are not susceptible to pitting attack. The following is quoted directly from his article:

At the commencement of the anodization, the following event occurs parallel to the other parent reactions, e.g. oxide growth and/or oxygen evolution:

followed by the dissolution, partial or complete, of the chloride

The M^{n+} in solution now undergoes complex formation:

where m is the coordination number of the metal.

For metals like Mo, Zr, Ti, etc., this $(M_n Cl_m)^{(m-n)e}$ complex is so stable that it effectively scavenges the Cl^- and thus prohibits them from further participation in the anodic charge transfer event [i.e. Equation (1)]. However, for the cases of Fe and Al, the lower stability of the outer orbital hybridization favors dissociation of the type:

Such a dissociation would make the free Cl^- ions available again to participate in the cycle [Equations (1-3)] that results in the dissolution of the metal.

Vijh's article³⁶ does not postulate any clear mechanism for reaction (1); it is not clear, for example, how chloride penetrate through the oxide film or how it liberates the metal ion. Also it is not clear why all chloride ions will be scavanged at metal-oxide interface.

The degree of susceptibility of a metal or alloy to pitting can be investigated by the following methods: (1) counting the number and measuring the depth and width of pits found in a suitable standard solution. (2) Determining the minimum concentration of Cl^- ions in solution causing pitting. (3) Determining the Breakdown Potential.

The method used in this investigation is the determination of breakdown potential (E_B). This method of screening alloys for pitting is new and has not yet been standardized by either American Society of Testing Materials or the National Association of Corrosion Engineers, but reviewing the very recent literature^{11,37,38} indicates its widespread use.

Wilde,³⁸ to prove the validity of this method, has compared predicted behavior of alloys based on their breakdown potential with previously published data on the same materials after prolonged exposure to a marine environment. According to him exact correlations have been observed between the two. Jackson³⁹ also has reported that good correlation exists between the electrochemical test and actual corrosion performance near the ocean.

There are reports that breakdown potential as measured by electrochemical methods might depend on metal surface preparation and/or on type of purifying gas.^{40,41} This problem, if it exists,

can be minimized by using a uniform method of surface preparation and the same purifying gas for all alloys to be tested. Results obtained in this investigation have shown that experimental E_p values are very reproduceable.

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GAGE LENGTH = 1"
THICKNESS = 0.08"
SCALE: 2" = 1"

FIG. 1 DIMENSIONS OF TENSILE SPECIMEN.

XBL 724-6149

FIG. 2 SCHEMATIC ANODIC POLARIZATION CURVE OF AN ACTIVE - PASSIVE METAL.

XBL724-6150

FIG. 3 SCHEMATIC DIAGRAM OF POLARIZATION CELL.

XBL 724-6151

FIG. 4 WORKING-ELECTRODE ASSEMBLY.

XBL724-6201

FIG. 5 SCHEMATIC DIAGRAM OF POLARIZATION APPARATUS.

XBL 724-6152

FIG. 6 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR STAINLESS STEEL 304 IN 1N H₂SO₄ AT 25°C.

XBL 724-6153

FIG. 7 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR STAINLESS STEEL 316
IN 1N H₂SO₄ AT 25°C.

XBL724-6154

FIG. 8 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN 2N H₂SO₄ AT 25°C.

XBL 724-6455

FIG. 9 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOY A IN H_2SO_4 AT 25°C .

XBL 724-6156

FIG. 10 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOY A₁₀ IN 1N H₂SO₄ AT 25°C.

XBL724-6157

FIG. 11 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOY A₂₀ IN 1N H₂SO₄ AT 25 °C.

XBL 724-6158

FIG. 12 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOY A₃₀ IN 1N H₂SO₄ AT 25°C.

XBL724-6159

FIG. 13 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
0.5 N H_2SO_4 + 0.25 N NaCl AT 25°C.

XBL 724-6160

FIG. 14 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
IN $\text{H}_2\text{SO}_4 + 0.25\text{ N NaCl}$ AT 25°C .

XBL724-6161

FIG. 15 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
2N H_2SO_4 + 0.25N NaCl AT 25°C.

XBL724-G62

FIG. 16 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
0.1 N H_2SO_4 + 0.5 N NaCl AT 25°C.

XBL724-6163

FIG. 17 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
0.5N H₂SO₄ + 0.5N NaCl AT 25°C.

XBL724-6164

FIG. 18 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY B IN
1N H₂SO₄ + 0.5N NaCl AT 25°C.

XBL 724-6165

FIG. 19 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOY B AND STAINLESS STEEL 316 IN ARTIFICIAL SEA-WATER AT 25°C.

XBL 724-6166

FIG. 20 POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR ALLOYS A₀ AND A₂₀ AND STAINLESS STEEL 316 IN ARTIFICIAL SEA-WATER AT 25 °C.

XBL 724-6167

FIG. 21 POTENTIODYNAMIC ANODIC POLARIZATION CURVE FOR ALLOY C IN
1N H_2SO_4 AT 25°C .

XBL 724-6168