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ABSTRACT

Anodic polarization tests on certain metastable austenitic ("TRIP") steels having very high strength and good ductility indicate that, with contents of sulfur, phosphorus, and other impurities comparable to those of commercial alloy steels, they would have about the same general corrosion resistance as commercial Type 316 stainless steel and appreciably better resistance to pitting in sea water. Cold-working of a TRIP steel increased its resistance to pitting somewhat and decreased its indicated general corrosion resistance slightly; these effects appear to be due to the transformation of austenite to martensite as a result of the cold-working rather than to the cold-working itself.

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INTRODUCTION

"TRIP" steels are a recently developed class of steels which, by virtue of appropriate composition and thermomechanical processing, have both very high strength and good ductility.[1] Such steels are austenitic, but during deformation at service temperature they transform to martensite (whence the name TRIP, from "transformation-induced plasticity").

An earlier investigation on TRIP steels made of high-purity constituents[2] showed that certain of the steels not only had excellent mechanical properties but also had general corrosion resistance, as indicated by anodic polarization tests, comparable to that of type 316 stainless steel. The present investigation was undertaken to determine the effects on such TRIP steels of (a) the presence of impurities (S, P, Mn, Si, etc.) at levels comparable to those in commercial steels, (b) the transformation of austenite to martensite by cold-working, and (c) chloride solutions, including artificial sea water.

ALLOYS INVESTIGATED

To prepare the TRIP steels, the constituents were induction-melted and poured into copper molds in an argon atmosphere. The resulting 16-pound ingots were forged at 1100°C into bars 2 inches wide and 0.8 inch thick, which were cross-rolled at 1100°C into bars 0.5 inch thick. The latter were austenitized for 90 minutes at 1200°C and quenched in ice brine. The thermomechanical treatment consisted of repeatedly heating the 0.5 inch bars to 500°C and passing them through heated rolls until a final thickness of 0.1 inch (80% reduction in thickness) was attained.

The chemical analyses of the TRIP steels and of specimens of commercial Types 304 and 316 stainless steel tested for comparison are given in Table I. The TRIP steels all contained 13% Cr, 11% Ni-plus-Mo, and 0.23 ± 0.02% C. Alloys 3Mo and 4Mo were used because the previous work had shown them to have an excellent combination of mechanical properties and general corrosion resistance, and alloy 5Mo was used to provide further information on the effect of molybdenum content; these three alloys were made of high-purity constituents. Alloy 4MoX was similar to 4Mo except for contents of S, P, Mn, Si, and undetermined residual elements, and was made by melting commercial AISI 4130 steel with appropriate additions of Cr, Ni, Mo, and Mn.

The tensile properties of the TRIP steels, measured on an Instron testing machine at a crosshead speed of 0.02 cm/min, together with their hardnesses, are summarized in Table 2. All show very high strength and good ductility.

TABLE I. Chemical Analyses of Steels Tested

Alloy	%Cr	%Ni	%Mo	%C	%Mn	%P	%S	%Si
3Mo	13	8	3	0.24	<0.01	0.001	0.012	0.04
4Mo	13	7	4	0.23	<0.01	0.002	0.008	0.02
4MoX	13	7	4	0.21	1.0	0.006	0.025	0.18
5Mo	13	6	5	0.25	<0.01	0.004	0.008	<0.02
304	20	8	0.4	0.06	1.4	0.02	0.036	0.60
316	17.5	13.5	3	0.05	1.0	0.01	0.012	0.49

TABLE II. Mechanical Properties of TRIP Steels

Alloy	Yield strength, psi	Tensile strength, psi	Elong. in 1 inch, %	Reduction in area, %	Hardness, Rockwell C
3Mo	187,000	231,000	38	38	45
4Mo	170,000	251,000	30	43	48
4MoX	194,000	245,000	32	39	51
5Mo	170,000	277,000	19	19	53

TEST PROCEDURE

Corrosion resistance was evaluated at 22° ±1°C by means of potentiodynamic anodic polarization tests, using an instrument arrangement similar to that described by France and Lietz,[3] a polarization cell as recommended by ASTM,[4] and a specimen holder similar to that described by Myers et al.[5] The test solutions were prepared from reagent-grade chemicals and double-distilled water, and (except for artificial sea water) were purged with hydrogen before and during the tests. The voltage was scanned in the noble direction at the rate of 1.4 volts per hour, starting within 10 mv of open-circuit voltage. Polarization potentials were measured against a saturated calomel electrode (SCE).

GENERAL CORROSION RESISTANCE

The polarization curves for the various steels in 1 N H_2SO_4 solution* are shown in Figure 1. The major parameters (I_c, critical current density; I_p, passive current density; and E_{pp}, primary passive potential)

*Steel 3Mo was measured in 2 N H_2SO_4 solution, but the results would not have been greatly different in 1 N H_2SO_4.

are summarized in Table III; I_c and I_p were reproducible to ±10% and E_{pp} to ± 0.01 volt. From these results, alloys 3Mo, 4Mo, and 5Mo may be expected to be considerably better with respect to general corrosion resistance than the Type 304 stainless steel specimen, alloys 4Mo and 5Mo slightly better than the Type 316, and alloy 4MoX, with "commercial" contents of S, Mn, etc., about the same as the Type 316. Wilde and Greene,[6] from a statistical analysis of similar tests on Types 304 and 316 steels from many heats, concluded that Mn and especially S tend to increase the critical current density I_c, that Mo, Cr, and C tend to lower I_c, and that P, Ni, and Si have little effect. Troselius,[7] from a somewhat similar analysis of tests on many specimens of various types of stainless steels, found similar correlations for Mn, S, Mo, and Cr, but reports that Si tends to increase I_c, that P and Ni tend to lower it, and that C has little effect. The data in Table III cannot be evaluated, therefore, in terms of the chemical composition of the alloys (except for the expected beneficial effect of Mo), but it may be concluded that the general corrosion resistance of commercial TRIP steels similar in composition to alloy 4MoX would be comparable to that of commercial Type 316 stainless steel.

EFFECTS OF COLD WORK

To transform the austenite in TRIP steel 4Mo partly to martensite, three pieces of the 0.1 inch thick material were rolled at room temperature, the thickness being reduced by 10, 20, and 30 percent, respectively. The martensite content of each was then determined by measurement of magnetic

TABLE III. Anodic Polarization Parameters of Steels in 1 N H_2SO_4 Solution.

Steel	E_{pp} v (SCE)	I_c $\mu A/cm^2$	I_p $\mu A/cm^2$
304	-0.24	76	8
3Mo*	-0.22	17	6
4MoX	-0.20	11	5
316	-0.22	12	4
4Mo	-0.22	6	4
5Mo	-0.18	6	2

*In 2 N H_2SO_4

saturation, and anodic polarization tests were made as before. The results, which are summarized in Table IV, show that 7% transformation had no appreciable effect and that 20% and 30% transformation caused relatively small increases in I_c and shifts in E_{pp} to more active potentials. These effects appear to be due to the transformation rather than to the cold work per se, since it must be remembered that in the thermomechanical treatment the alloy had already undergone 80% cold working at 500°C*.

Shortly after the experimental work reported here was completed, Elayaperumal et al[8] reported that 26% cold working of commercial Type 304 stainless steel had virtually no effect on its anodic polarization parameters, but that severe cold working (50% and 68%) caused a large increase in I_c, which they concluded was due to the formation of martensite.

*Such treatment is sometimes called "warm working" but is actually cold working, since it is carried out well below the recrystallization temperature of austenite. Cold work brings about the transformation of austenite to martensite only below a composition-dependent critical temperature M_d.

TABLE IV. Effects of Cold Work on Anodic Polarization Parameters of TRIP Steel 4Mo in 1 N H_2SO_4 Solution

Cold work %	Martensite %	E_{pp} v (SCE)	I_c $\mu A/cm^2$	I_p $\mu A/cm^2$
0	0	-0.22	6	4
10	7	-0.20	6	4
20	20	-0.24	9	4
30	30	-0.26	11	4

PITTING CORROSION

In anodic polarization curves of active-passive metals susceptible to pitting corrosion, a sharp rise in current density appears at a potential (the "breakdown potential" E_b) less noble than the normal transpassivation potential. Wilde and Williams[9] have recently shown an excellent correlation of the magnitude of the breakdown potential of various stainless steels with their resistance to pitting in long-term corrosion tests. Szklarska-Smialowska has reviewed the recent literature on pitting corrosion.[10]

Anodic polarization parameters for the various steels in air-saturated artificial sea water ("substitute ocean water" with pH 8.2 prepared according to ASTM specifications[11]) are given in Table V, and most of the curves from which the data were taken are shown in Figure 2. The parameters in Table V include the breakdown potential E_b, taken as the potential at which the current density had risen to 40 $\mu A/cm^2$[7]; E_b was reproducible to about $\pm$ 0.03 volt. The critical and passive current densities, I_c and I_p, do not differ greatly from those in 1 N H_2SO_4 solution (Tables III and IV) and show similar trends.

The breakdown potentials of the TRIP steels in the artificial sea water increase with their Mo content, as has been observed with other alloys[10]; alloy 5Mo, in fact, shows no breakdown, its curve being similar to that in 1 N H_2SO_4 solution, so it probably would not be susceptible to pitting. The value of E_b for alloy 4MoX, containing commercial contents of impurities, is slightly lower than that for the corresponding high-purity alloy 4Mo, but is substantially higher than that for the Type 316 stainless steel. Cold working of alloy 4Mo appreciably increased its breakdown potential; since cold working has little effect on the corrosion-resistance properties of austenitic stainless steels,[10] it again appears that its effects on the corrosion-resistance properties of the TRIP steels is due to the transformation of austenite to martensite and not to the cold work as such.

TABLE V. Anodic Polarization Parameters of Steels in Air-Saturated Artificial Sea Water

Steel*	E_{pp} v (SCE)	E_b v (SCEP)	I_c $\mu A/cm^2$	I_p $\mu A/cm^2$
316	-0.29	0.31	6	4
3Mo	-0.23	0.45	10	8
4MoX	-0.24	0.55	12	7
4Mo	-0.25	0.68	8	4
4Mo(10)	-0.15	0.76	14	10
4Mo(20)	-0.22	0.85	10	7
4Mo(30)	-0.22	0.80	11	9
5Mo	-0.14	**	8	4

*Parentheses indicate percent reduction in thickness by cold work.

**No breakdown.

In Table VI are summarized the results of tests on alloy 3Mo in hydrogen-saturated NaCl-H_2SO_4 solutions of various concentrations. No breakdown occurred in the 0.25 N NaCl solutions, even at an acid concentration as high as 2N. In 0.5 N NaCl, however, breakdown occurred at the lowest acid concentration tested, 0.1 N, and E_b decreased rapidly with increasing acidity. The critical chloride ion concentration, below which breakdown does not occur, is thus between 0.25 and 0.5 N, well above the value of 0.1 N reported, for example, for a stainless steel containing 18.6% Cr and 9.9% Ni.[10] The data in Table VI show also that, within the ranges tested, E_{pp} is independent of acid concentration but is shifted strongly to more active potentials by increase in NaCl concentration, I_c increases rapidly with increase in concentration of either NaCl or H_2SO_4, and I_p is independent of the concentration of either.

TABLE VI. Anodic Polarization Parameters of TRIP Steel 3Mo in NaCl-H_2SO_4 Solutions

NaCl N	H_2SO_4 N	E_{pp} v (SCE)	E_b v (SCE)	I_c μA/cm^2	I_p μA/cm^2
0.25	0.50	-0.27	*	43	4
0.25	1.00	-0.26	*	280	4
0.25	2.00	-0.26	*	450	4
0.50	0.10	-0.37	0.66	35	4
0.50	0.50	-0.36	0.41	190	4
0.50	1.00	-0.37	0.38	700	4

*No breakdown.

SUMMARY

Potentiodynamic anodic polarization tests were made on specimens of four metastable austenitic ("TRIP") steels having very high strength

and good ductility and, for comparison, on specimens of commercial Types 304 and 316 stainless steel. Three of the TRIP steels, designated 3Mo, 4Mo, and 5Mo, were high-purity alloys containing, respectively, 3, 4, and 5% Mo and 8, 7, and 6% Ni, together with 13% Cr and 0.23 $\pm$ 0.02% C; the fourth, designated 4MoX, was similar to 4Mo but was made largely from a commercial alloy steel, so that it contained S, P, Mn, Si, and underdetermined residual elements at concentrations comparable to those in commercial alloy steels. The results are as follows:

1. The critical and passive current densities indicate that, with respect to general corrosion resistance in dilute sulfuric acid or in artificial sea water, all four TRIP steels were superior to the Type 304 stainless steel, alloys 4Mo, 5Mo, and 4MoX being at least comparable to the Type 316.

2. The four TRIP steels had appreciably higher breakdown potentials in artificial sea water than the Type 316 stainless steel, indicating better resistance to pitting. Alloy 5Mo, in fact, showed no breakdown, so it may not be susceptible to pitting in sea water.

3. After alloy 4Mo had been cold rolled so that up to 30% of the austenite was transformed to martensite, its breakdown potential in artificial sea water increased and its indicated general corrosion resistance in dilute sulfuric acid or in artificial sea water decreased slightly. These effects appear to be due to the transformation rather than to the cold working as such.

4. Alloy 3Mo showed breakdown in 0.50 N NaCl solutions at low H_2SO_4 concentrations but not in 0.25 N NaCl solutions at relatively high H_2SO_4 concentrations.

ACKNOWLEDGMENTS

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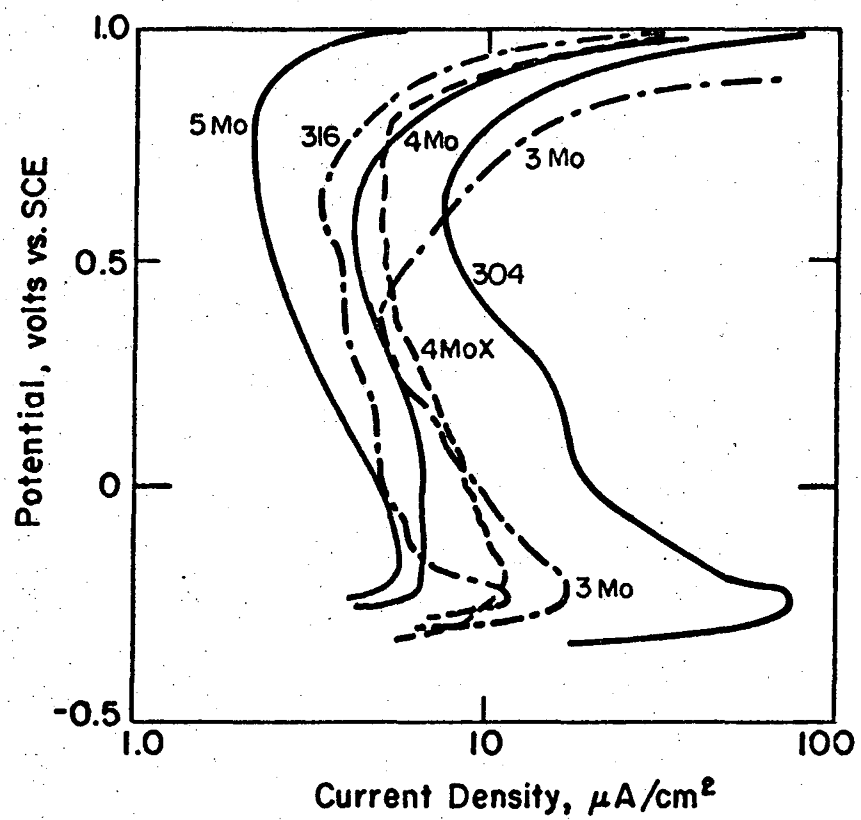
REFERENCES

1. V. F. Zackay, E. R. Parker, D. Fahr, and R. Busch, Trans. ASM, 60 252 (1967).
2. F. Padilla, J. F. Challande and S. F. Ravitz, UCRL Report 19657, Lawrence Berkeley Laboratory, Univ. of Calif., Berkeley, Calif. (1970).
3. Metals Handbook, 8th Ed., 1, p. 414, American Society for Metals, Metals Park, Ohio (1961).
4. W. D. France, Jr. and R. W. Lietz, Corrosion, 24, 298 (1968).
5. Standard G5-71, Annual Book of ASTM Standards, 1971, Part 31.
6. J. R. Myers, E. G. Gruenler and L. A. Smulczenski, Corrosion, 24, 352 (1968).
7. B. E. Wilde and N. D. Greene, Jr., Corrosion, 25, 300 (1969).
8. L. Troselius, Corrosion Science, 11, 473 (1971).
9. K. Elayaperumal, P. K. De, and J. Balachandra, Corrosion, 28, 269 (1972).
10. B. E. Wilde and E. Williams, J. Electrochem. Soc., 118, 1057 (1971).
11. Z. Szklarska-Smialowska, Corrosion, 27, 223 (1971).
12. Standard D1141-52, Annual Book of ASTM Standards, 1971, Part 23.

FIGURE CAPTIONS

Fig. 1 Potentiodynamic anodic polarization curves of steel specimens in 1 N H_2SO_4 solution (2 N H_2SO_4 for specimen 3Mo).

Fig. 2 Potentiodynamic anodic polarization curves of steel specimens in air-saturated artificial sea water.



XBL 7311-6637

Fig 1.

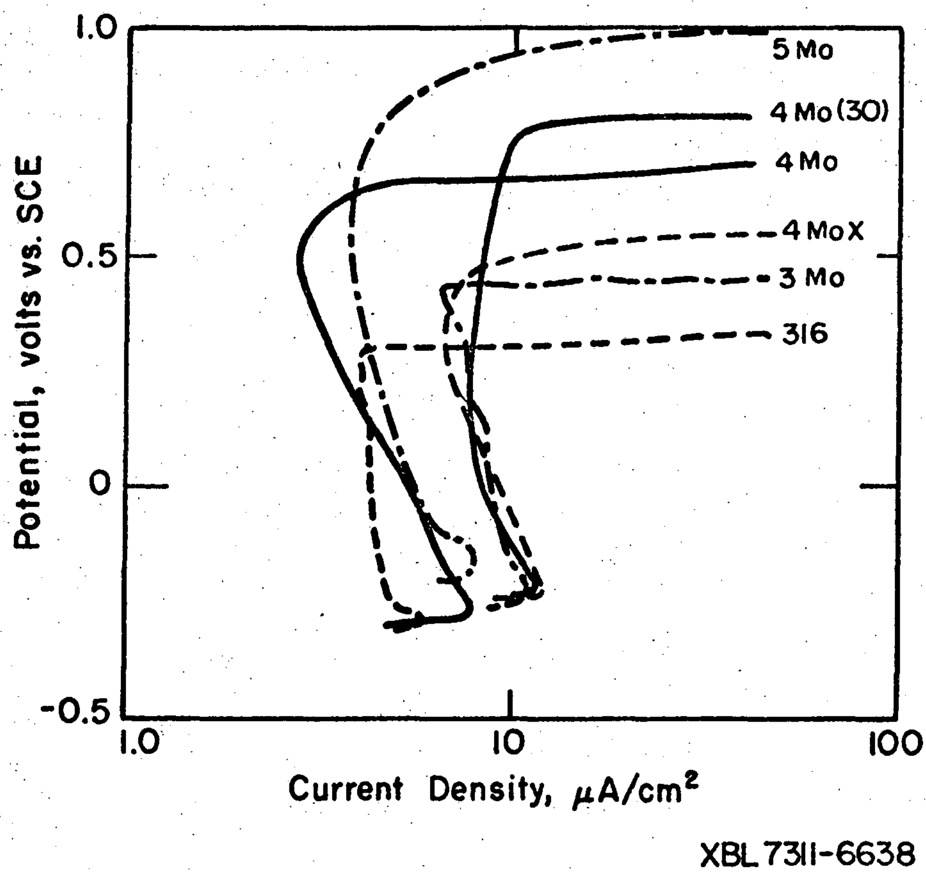

1.0
0.5
0
-0.5
Potential, volts vs. SCE
1.0
10
100
Current Density, μA/cm²
5 Mo
4 Mo (30)
4 Mo
4 MoX
3 Mo
316
XBL 7311-6638

Fig. 2.