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ELASTIC AND PLASTIC STRAINS AND THE STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

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ABSTRACT

The influence of homogeneous (uniformal tension) and heterogeneous (rolling) deformation on the SCC of a transformable (301) and a non transformable (310) stainless steel in 30% MgCl_2 has been under study. The amount or type of deformation with or without the presence of deformation induced martensite did not appear to influence the electrochemical parameters such as the rest potential or the critical cracking potential. Metallographic studies combined with failure tests and polarization curves identified the pitting potential with the critical cracking potential and indicated that the cracking potential was merely that for initiation of cathodic protection; that is the potential at which the current changes from anodic to cathodic.

The failure time at constant applied stress increased significantly with amount of deformation indicating a maximum or optimum amount of plastic deformation. For tests conducted at a fixed percentage of the yield strength, the failure time decreased with increased amounts of deformation, independent of the type of deformation.

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INTRODUCTION

This program is concerned with the SCC of plastically deformed austenitic stainless steels in chloride environments. Previous work (1) examined the influence of deformation on failure in boiling 3% NaCl solutions and demonstrated that classical SCC did not occur in this environment. Rather, dissolution (primarily by pitting) reduced the cross sectional area to the point that overload, ductile failure occurred in the conventional manner. Consequently, work during the past year has concentrated on a more aggressive environment - 30% MgCl_2 boiling at 115°C .

The principal parameters under study during the past year were:

- a. Homogeneous deformation without transformation (310)
- b. Heterogeneous deformation without transformation (310)
- c. Heterogeneous deformation with transformation (301)

The influence of these deformation and structural parameters were examined on the following aspects of SCC:

- A) Corrosion potential - E_{oc}
- B) Critical cracking potential - E_c
- C) Breakdown potential for pitting - E_b
- D) Repassivation potential for pitting - E_p
- E) Time to fail as a function of potential

EXPERIMENTAL

Analysis of the three steels employed in this study are presented in Table 1. The 301 and 310 stainless steels were employed for the study of the effects of structure and deformation on SCC in MgCl_2 and the 304 stainless steel was used in an exploratory study of the possibility of producing SCC in a saturated solution of NaCl.

The influence of deformation on the yield strength of 301 and 310 and on the amount of martensite formed in 301 is presented in Tables 2 and 3. The electrochemical and mechanical testing techniques employed in this study have been described previously and need not be repeated here. All SCC tests were performed in uniaxial tension and loads as well as potentials were applied one hour after immersion in the test solution in order to allow a more or less stable rest potential to be achieved.

RESULTS AND DISCUSSION

The MgCl_2 solution that has been widely employed in the literature contains 42% MgCl_2 and boils at 145°C . Partial solidification at room temperature complicates the use of this solution at potentials other than the rest potential. Consequently, the behavior in 30% MgCl_2 was compared with that in the 42% solution in a series of preliminary experiments. Figs. 1 and 2 compare the performance of an annealed 310 in the two solutions. Although failure times in the 30% MgCl_2 solution are somewhat longer than in the 42% MgCl_2 solution, the electrochemical parameters were virtually the same in both solutions. In both cases, the rest potential was -330 MV (SCE) and the critical cracking potential was approximately -340 MV (SCE). Consequently, the 30% MgCl_2 solution was selected for study of the influence of deformation on SCC. This solution boils at 115°C .

Failure time - potential curves analogous to those of Figs. 1 and 2 were determined and used to evaluate the influence of deformation on SCC. It is apparent in Figs. 1 and 2 that the behavior is characterized by a critical cracking potential - E_c with failure occurring when the sample is anodically polarized relative to this cracking potential. Tables 4 & 5 summarize the influence of deformation of the cracking potential and the rest potential of 310 in deaerated 30% MgCl_2 .

Within the reproducibility of these measurements, neither the type of deformation (uniaxial tension versus rolling) nor the amount of deformation influence either the rest potential or the cracking potential. Thus, for these austenitic stainless steels in the concentrated chloride solution, the open circuit and cracking potentials

are independent of elastic strains (1) as well as plastic strains. This of course, does not deny the substantial role that residual stresses play in different environments.

These results indicate that the electrochemical parameters in this environment are determined by the properties of a filmed surface. Although highly localized breakdown (pseudopassivity) of this film associated with pits does occur, the film separates the electrolyte from the base metal over virtually the entire surface. Thus the electrochemical parameters are independent of the deformation state of the underlying substrate. Whether or not this conclusion also applies to other environments such as H_2SO_4 - NaCl in which SCC occurs in the active rather than the passive or pseudo-passive range (2) deserves evaluation.

In contrast to the electrochemical parameters, the time to fail at the rest potential is sensitive to the amount of deformation and, of course, to the applied stress. Typical data are represented in Tables 6 and 7 and the effects of the deformation modes on time to fail are compared in Fig. 3. The increased failure time with reduction in applied load is evident in the relative behavior of tests conducted at 70% of the Y. S. compared with those at 90% of the Y.S.

Tests conducted at 70% of the yield strength reveal clearly that the failure time (at constant fraction of the yield strength) is reduced by plastic deformation. On the other hand, the failure time at constant applied stress increases significantly with amount of deformation as indicated by the data of Fig. 4. This effect has been reported in the literature for other environments (3). The maximum at intermediate deformations is significant and has also been observed in less aggressive environments (4). It also is apparent in Fig. 3 that the mode of deformation does not influence time to fail when tests were conducted at 70% of the yield strength.

For tests conducted at 90% of the yield strength, the failure time was less sensitive to the amount of deformation. The insensitivity to deformation exhibited by the rolled materials is under further study.

Thus, it appears that there is a critical amount of deformation for optimum resistance to SCC. In short, this suggests that the resistance to SCC of deformed austenitic stainless steels involves compromise with strength level attained by the deformation. This concept is under further examination.

The 301 steel was employed to evaluate the influence of deformation induced martensite on SCC in 30% MgCl_2 . All deformations were produced by rolling and typical data on the rest potential and cracking potential are presented in Table 8. Both the rest and cracking potentials in this 301 stainless steel are approximately 30 MV more active than the corresponding values for the non-transforming 310 stainless steel. This does not appear to be associated with martensite formation since the annealed 301 exhibited the same behavior; an unexpected observation, the general nature of which will be examined in other environments. As shown in Table 9, the rest and cracking potentials were not influenced by aeration (oxygen).

The influence of deformation on time to fail at the rest potential is presented in Table 10 and Fig. 5. As with the non-transforming 310 stainless steel, the failure time at a constant fraction of the yield strength is reduced by plastic deformation. The failure time in this 301 steel appears to be less sensitive to applied load in the range from 70% to 90% of the yield strength than does 310. The reason for this is not apparent and requires further study. As shown in Fig. 6, failure time exhibits an equally good correlation with percent martensite in this 301 stainless steel. Since however, the amount of martensite increases with amount of

deformation, it seems most likely that the behavior in Fig. 6 simply reflects the increased strength produced by deformation. That is, martensite formation does not appear to exert a significant role in this environment.

It has been difficult to evaluate the influence of deformation on the pitting potentials in these steels. Metallographic examination indicated that pitting occurred at the rest potential and at all potentials where SCC occurred. Current-time relationships indicated that cracking was invariably associated with anodic currents and that cathodic currents provide immunity. Metallographic studies also demonstrated that samples polarized at potentials cathodic to the cracking potential were free of pits. This identifies the cracking potential with the pitting potential in these stainless steels and this environment. It has not been possible to distinguish between the breakdown potential and the re-passivation potential because there is no passivity. The identification of the pitting potential with the cracking potential, however, indicates that the pitting potential also does not depend on the state of deformation in this environment. This also has been reported for NaCl environments (5).

It appears from these results that the aggressivity of the MgCl_2 is too severe resulting in pitting at the open circuit condition. This may mask more subtle effects on SCC produced by the amount or type of deformation as well as partial transformation to martensite. This aggressivity is revealed clearly in the polarization behavior shown in Fig. 7. Anodic polarization results in immediate increase to high current densities as a result of pitting at the open circuit potential. It also is apparent from the cathodic polarization curve that there is virtually no range of low current density characteristic of a truly stable passive state.

Although it was not possible to obtain SCC of 310 stainless steel in 3% NaCl, the possibility that cracking may occur in more concentrated solutions deserves more detailed study. Preliminary results on a 304 stainless steel tested in aerated saturated NaCl are presented in Table 11 and Fig. 8. It is apparent that a critical cracking potential exists at -410 MV although the failure times are significantly longer than in the MgCl_2 solution. The SEM photos of Fig. 9 compare the fracture characteristics of 301 tested in MgCl_2 and 304 in saturated NaCl. The similarities in fracture characteristics are apparent with predominately transgranular SCC occurring in both solutions. Thus the NaCl environment appears to offer considerable promise for more detailed study of the effects of deformation on SCC.

CONCLUSIONS

The influence of homogeneous (prestrain in uniaxial tension) and heterogeneous (prestrain by rolling) deformation on the SCC of a nontransformable (310) and a transformable (301) stainless steel has been evaluated in deaerated 30% MgCl_2 , boiling at 115°C . Neither the amount or type of deformation nor the presence of martensite influenced the electrochemical parameters - rest potential, pitting potential or critical cracking potential. The electrochemical parameters appear to be determined by the properties of a filmed surface and consequently are not influenced significantly by the state of the underlying substrate. It is believed that this is largely the result of the aggressive nature of the boiling MgCl_2 environment.

Metallographic studies indicated that pits were associated with cracks at all potentials anodic to the cracking potential and that samples polarized cathodic to the cracking potential were free of pits. This identifies the cracking potential with the pitting potential for the conditions examined in this study.

At a constant applied stress, there appears to be an optimum amount of deformation which significantly increases the resistance to SCC. However, at a constant percentage of the yield strength, the time to fail decreased with increasing deformation, independent of the mode of deformation for 301 stainless.

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TABLE 1

COMPOSITIONS (%)

<u>TYPE S.S.</u>	<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>C</u>	<u>Mo</u>	<u>Si</u>	<u>Cu</u>	<u>N</u>	<u>P</u>	<u>S</u>	<u>Co</u>
310	24.57	19.68	1.62	.055	.22	.52	.25	.017			
301	17.63	7.22	.79	.079	.13	.54	.17		.030	.015	.09
304 *	18.39	9.5	.87	.064	.61	.57	.24		.039	.013	.13

* YIELD STRENGTH ANNEALED - 45.6 KSI

Table 2:310 S.S. Yield Strength

Uniaxial		Rolled	
% Def	Y.S. KSI	% Def	Y.S. KSI
0	29	10	80
10	64	20	98
20	88	30	114
30	103	38	127

Table 3:

Yield Strength & % Martensite
in cold rolled 301

% Def	Y.S. KSI	% Mart.
0	40	0
10	72	5
20	116	15
30	148	>20

Table 4: Average Eoc & Ecc
 310 Uniaxially Deformed
 Deaerated 30% MgCl_2 pH 4.5 115°C
 Loaded to 90% Yield Strength

% Def	Ave.Eoc (MV SCE)	Ecc (MV SCE)
0	-335	-345
10	-331	-360
20	-350	-355

Table 5: Average Eoc & Ecc
 310 Rolled Deaerated 30% MgCl_2 pH 4.5 115°C
 Loaded to 90% Yield Strength

% Def	Ave.Eoc (MV SCE)	Ecc (MV SCE)
10	-340	-345
20	-340	-355
38	-335	-355

Table 6: Eoc & Time to Fail
 310 Uniaxial Open Circuit
 Deaerated 30% MgCl_2 pH 4.5 115°C

% Def	90% Y. S.		70% Y. S.	
	Eoc (MV)	TTF (hrs.)	Eoc (MV)	TTF (hrs.)
0	-330	7.6	-339	80.6
			-335	58.8
10	-330	7.4	-334	33.7
			-338	30.2
20	-330	1.5	-335	20.2
30			-338	24.8

Table 7: Eoc & Time to Fail

310 Rolled Open Circuit

Deaerated 30% MgCl_2 pH 4.5 115°C

% Def	90% Y.S.		70% Y. S.	
	Eoc (MV)	TTF (hrs)	Eoc (MV)	TTF (hrs)
10			-340	39.5
20	-335	9.3	-335	21.7
30			-338	11.5
			-338	14.5
38	-325	7.6		

Table 8: Average Eoc & Ecc
 301 Heat Rolled
 Deaerated 30% Mg Cl₂ pH 4.5 115°C
 Loaded to 90% Yield Strength

% Def	Ave. Eoc (MV SCE)	Ecc (MV SCE)
0	-380	-385
10	-390	-383
20	-385	-375
30	-380	-388

Table 9 : Average Eoc & Ecc
 301 Heat Rolled pH 4.5 115°C
 Aerated 30% MgCl₂ 90% Yield Strength

% Def	Ave. Eoc (MV SCE)	Ecc (MV SCE)
0	-380	-375
10	-380	-375

Table 10: Eoc & Time to Fail
 301 Heat Rolled Open Circuit
 Deaerated 30% MgCl_2 pH 4.5 115°C

% Def	90% Y. S.		70% Y.S.	
	Eoc (MV)	TTF (hrs)	Eoc (MV)	Ttf (hrs)
0	-384	6.9	-380	28.0
10	-370	14.7	-370	5.4
20	-376	1.8	-375	2.5
30	-380	1.2	-370	1.4

Table 11:

Annealed 304

Average Eoc & Ecc

70% Yield Strength

Eoc & Time to Fail

90% Yield Strength

Aerated Saturated NaCl pH 6.5 105°C

70% Y.S.		90% Y.S.	
Ave. - Eoc (MV SCE)	Ecc (MV SCE)	Eoc (MV SCE)	TTf (Hrs.)
-382	-410	-360	185

FIG. 1: TIME TO FAIL VS. POTENTIAL
310 ANNEALED, 90% YIELD STRENGTH
DEAERATED 40% MgCl_2 , 145°C . PH4.5.

FIG 2.: TIME TO FAIL VS. POTENTIAL
 310 ANNEALED, 90% YIELD STRENGTH,
 DEAERATED 30% $MgCl_2$ 115° C, PH 4.5.

FIG. 3 310 TIME TO FAIL VS. % DEFORMATION
DEAERATED 30% $MgCl_2$, 115°C, PH 4.5.
OPEN CIRCUIT.

FIG. 4: 310 TIME TO FAIL VS. % DEFORMATION
DEAERATED 30% MgCl_2 115°C, PH 4.5.
OPEN CIRCUIT. 26.1 KSI.

FIG. 5: TIME TO FAIL VS % DEFORMATION
301 ROLLED AND ANNEALED
DEAERATED 30% $MgCl_2$ 115° C PH 4.5.

FIG. 6: TIME TO FAIL VS % MARTENSITE,
301 ROLLED AND ANNEALED,
DEAERATED 30% $MgCl_2$ 115° C PH 4.5.

FIG. 7: 310 CURRENT VS. POTENTIAL
DEAERATED 30% MgCl_2 , 115°C , PH 4.5.

FIG. 8: TIME TO FAIL VS POTENTIAL
304 ANNEALED, 70% YIELD STRENGTH,
AERATED, SATURATED NaCl
107° C PH 6.5

700X

301 0% -380 M.V. 7.2 hrs. to fail
30% NgCl_2 Deaerated

1000X

304 Sat NaCl
O.C. 185 hours to fail.

Fig. 9: S.E.M. Micrographs of fracture surfaces produced in MgCl_2 and NaCl.