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# THE ENVIRONMENTAL CRACKING SUSCEPTIBILITIES OF THREE HIGH-STRENGTH ALLOY STEELS

G.J. Biefer

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THE ENVIRONMENTAL CRACKING SUSCEPTIBILITIES OF  
THREE HIGH-STRENGTH ALLOY STEELS

by

G. J. Bieffer\*

ABSTRACT

Notched, fatigue pre-cracked specimens of three high-strength alloy steels (T-1, CHT-100 and 1% Cu-3.5% Ni), with yield strengths of about 690 MPa (100 ksi), were tested for susceptibility to environmental cracking (EC). The specimens were loaded to fracture as cantilevers, using a rising-load technique. Susceptibility was assessed by comparing the nominal stress intensity at fracture under dry conditions,  $K_{Ii}$  (dry), with the value obtained for specimens fractured in contact with 3.5% NaCl solution. The latter specimens were tested under free-corrosion (f.c.) conditions and also while cathodically protected (c.p.) by coupling to zinc.

For parent metal specimens, free-corrosion caused only a slight degradation of load carrying capability by EC with  $K_{Ii}$  (f.c.)/ $K_{Ii}$  (dry) ratios averaging 0.94 (0.88 to 0.99). For parent metal coupled to zinc,  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry) ratios averaged 0.75 (0.73 to 0.84), thus showing definite susceptibility to EC of the hydrogen embrittlement variety. Weld metal appeared to be even more susceptible than parent metal under these conditions, and also showed highly variable behaviour in that  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry) averaged 0.69 (0.44 to 0.97).

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\*Head, Corrosion Section, Physical Metallurgy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

It is concluded that these steels would be susceptible to EC, particularly in or near the welds, in severe hydrogen-embrittling applications. It is recommended that thorough field and laboratory testing precede the use of these steels in such applications.

SUSCEPTIBILITE DE TROIS ALLIAGES D'ACIER DE HAUTE  
RESISTANCE AU FISSURAGE ENVIRONNEMENTAL

par

G. J. Biefer\*

RESUME

Des spécimens entaillés, préfissurés par fatigue, de trois alliages d'acier de haute résistance (T-1, CHT-100 et 1% Cu - 3,5% Ni), dont les tensions de fluage sont d'environ 690 MPa (100 ksi) ont été testés pour déterminer leur susceptibilité au fissurage environnemental (FE). Les spécimens ont été chargés, jusqu'au point de rupture, en porte-à-faux, en utilisant une technique de soulèvement de la charge. La susceptibilité a été évaluée en comparant l'intensité d'effort nominal à la rupture dans des conditions à sec,  $K_{Ii}$  (à sec), avec la valeur obtenue pour les spécimens fracturés au contact d'une solution 3,5% NaCl. Ces derniers spécimens ont été testés sans protection spéciale contre la corrosion et également lorsqu'ils étaient cathodiquement protégés (c.p.) par couplage au zinc.

Dans le cas des spécimens de métaux base, la corrosion libre a provoqué seulement une légère fluctuation de la capacité de charge, par des rapports de FE de  $K_{Ii}$  (c.l.)/ $K_{Ii}$  (à sec) se situant en moyenne à 0,94 (0,88 à 0,99). En ce qui concerne le métal base couplé au zinc, les rapports  $K_{Ii}$  (c.l.)/ $K_{Ii}$  (à sec) se situaient en moyenne à 0,75 (0,73 à 0,84), indiquant ainsi une susceptibilité définie au fissurage environnemental, plus particulièrement à la fragilité par décapage. Le métal en fusion apparaît encore plus susceptible que le métal base dans ces mêmes conditions,

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\*Chef, Section de la corrosion, Laboratoires de recherche en métallurgie physique, Centre canadien de la technologie des minéraux et de l'énergie, Ministère de l'Énergie, des mines et des Ressources, Ottawa, Canada.

et montre également un comportement très variable dans le sens que le rapport  $K_{Ii}$  (c.l.)/ $K_{Ii}$  (à sec) se situe en moyenne à 0,69 (0,44 à 0,97).

On conclut que ces aciers seraient susceptibles au FE, plus particulièrement dans ou près des soudures, dans les applications sévères de fragilité par décapage. On recommande que d'autres essais en laboratoire et sur le terrain précédent l'utilisation de ces aciers pour de telles applications.

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## INTRODUCTION

Research at PMRL, related to the Canadian hydrofoil craft Bras d'Or, had shown by 1971 that high-strength steels with yield strength levels down to about 965 MPa (140 ksi) were susceptible to environmental cracking (EC) under hydrogen embrittling conditions[1]. Steels at a minimum yield strength level of 690 MPa (100 ksi) were being used in marine service by the Canadian Armed Forces in complex welded structures such as masts, launcher doors and flight decks. Protection against corrosion was provided by inorganic zinc coatings. On the Bras d'Or, such a coating on 18% Ni maraging steel (yield strength: 1724 MPa or 250 ksi) had proved sufficiently hydrogen-embrittling to cause a failure of the foils by EC subsequent to prolonged contact with sea water[2]. The Department of National Defence (DND) therefore requested that PMRL assess the susceptibility to EC of three quenched and tempered alloy steels with yield strengths of about 690 MPa (100 ksi). The steels were either currently in use or considered for future use in marine service. The research described herein was performed as part of the Utilization Activity of CANMET's Minerals Research Program under the title "Comparison of Copper-Nickel Steel with Commercially Available High-Strength Alloys". Its primary aim was to provide a knowledge base for Canadian industry in the development of high-strength materials for defence use.

With respect to industrial and military developments, it is generally recognized that there can be a distinct economic advantage to using higher-strength steels which permit a decreased weight of steel in a given structure. However, as the strength of steel is increased, weldability, notch sensitivity, and other related factors may become problems. In the present work, susceptibility to EC is examined as a possible limiting factor to the use of alloy steels with yield strengths of approximately 690 MPa (100 ksi).



## EXPERIMENTAL

### Steels

Two of the alloy steels, designated T-1 (United States Steel Co.) and CHT-100 (Canadian Heat Treaters Ltd.), were made to ASTM-A517 specifications. The third, designated 1% Cu-3.5% Ni, had been developed at PMRL and showed satisfactory weldability and good low-temperature properties[3].

The commercial steels were supplied by DND from stock as 12.5- and 25-mm (1/2- and 1-in.) plate. The 1% Cu-3.5% Ni steel was provided as plate at the same two thicknesses. Chemical composition and mechanical properties of the plates were not determined but information from manufacturer's brochures and PMRL's foundry section is presented in Tables 1 and 2. The results of hardness measurements made at PMRL are also given.

### Specimens

Test specimens were bars 150 to 200 mm (6 to 8 in.) in length, 9.4 mm (3/8 in.) wide, and had a machined depth somewhat smaller than the as-received plate thickness. As described previously, both the upper surface and the sides of each bar were notched [1,4]. The length of the bar lay in the rolling direction and the depth in the plate thickness direction. A pre-crack was produced in the upper notch by fatiguing prior to testing, using a Krouse plate fatigue tester.

To produce specimens containing a weld, two V-notched pieces of plate were welded together in the welding section of PMRL, using identical procedures for the three alloys. The process was automatic gas metal-arc with an argon-2% O<sub>2</sub> mixture. The welding electrode used was purchased to meet MIL Type 120S-1 of Specification MIL-E-23765/2 (Ships) which requires weld tensile specimens to have a minimum ultimate tensile strength of 827 MPa (120 ksi) and a yield strength of 724 to 841 MPa (105 to 122 ksi).

Weld specimens were cut so that the weld was at the specimen centre, the bead lying transverse to the specimen length. Top and side notches were placed on the weld centre plane. Determinations of weld metal hardness for each of the three steels appear in Table 2.

Methods

As described previously, specimens were clamped to a solid post at one end and to a cantilever arm at the other[1,4]. A load rising at a pre-selected constant rate was then applied to the end of the cantilever arm, eventually causing fracture of the specimen. Nominal fracture toughness  $K_{Ii}$  (dry) was first obtained by fracturing specimens in air at a fairly rapid loading rate of  $>220 \text{ MPa}\sqrt{\text{m}}/\text{hr}$  ( $>200 \text{ ksi}\sqrt{\text{in.}}/\text{hr}$ ). Specimens were then tested which had the notch area immersed in replenished 3.5% NaCl solution either freely corroding to determine  $K_{Ii}$  (f.c.), or cathodically protected by a zinc sacrificial anode (about -1.05 V SCE) to determine  $K_{Ii}$  (c.p.). Specimens immersed in 3.5% NaCl were loaded at the much lower rate of  $<0.66 \text{ MPa}\sqrt{\text{m}}/\text{hr}$  ( $<0.6 \text{ ksi}\sqrt{\text{in.}}/\text{hr}$ ). EC susceptibility was demonstrated in terms of the values of the ratios  $K_{Ii}$  (f.c.)/ $K_{Ii}$  (dry) and  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry).

The equations used in calculating the nominal stress intensity  $K_{Ii}$  were those developed by workers at the U.S. Naval Research Laboratory, Washington, D.C.[5,6]:

$$K_{Ii} = \left( \frac{B}{B_N} \right)^{1/2} \frac{\beta M}{BD^{3/2}} \dots \dots (1)$$

Here, B is the specimen width of 9.4 mm (3/8 in.), and  $B_N$  is the width measured at the side notches. D is the specimen depth. M is the bending moment at the notch, i.e., the cantilever arm length multiplied by the effective force at the end of the arm. The factor  $\left( \frac{B}{B_N} \right)^{1/2}$  is a correction for the effect of the side notches.

The factor  $\beta$  is a function of the notch plus the pre-crack depth "a" and the specimen depth D. It is defined by

$$\beta = 4.12 \sqrt{\frac{1}{(1 - a/D)^3} - (1 - a/D)^3} \dots (2)$$

In all cases,  $K_{Ii}$  at fracture was evaluated in terms of the specimen geometry at the start of the test, i.e., that of the fatigue pre-cracked specimen, calculated using measurements of "a" made after the specimen had been fractured.

### RESULTS

The results obtained in the rising-load tests are presented in Tables 3 to 5 in terms of nominal stress intensities at fracture. The approximate ratios between the individual  $K_{Ii}$  (f.c.) and  $K_{Ii}$  (c.p.) values and the corresponding average  $K_{Ii}$  (dry) value are also presented.

Free-corrosion conditions were investigated for the 12.5-mm (1/2-in.) thick parent metal plate. It was found that  $K_{Ii}$  (f.c.)/ $K_{Ii}$  (dry) ratios for the three steels were similar, averaging 0.94 (0.88 to 0.99). This comparatively slight degradation by EC was near the limit of sensitivity of the method used, and additional free-corrosion measurements were not performed on the 25-mm (1-in.) thick steels.

For parent metal specimens, coupling to zinc produced a more definite decrease in load-carrying ability. Excluding the 25-mm (1-in.) 1% Cu-3.5% Ni steel, which will be discussed below, the  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry) ratios averaged 0.79 (0.73 to 0.84) and the three steels were not greatly dissimilar in behaviour. Weld metal specimens, under zinc-coupling, showed greater degradation by EC than parent metal, and also more variability in their behaviour. Here, the  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry) ratio averaged 0.69 (0.44 to 0.97).

All fractured specimens were examined using a stereomicroscope with a maximum magnification of 40X. The fracture faces were approximately flat, but showed curvature at the sides, indicative of necking. This was most evident in parent metal

specimens of the 25-mm (1-in.) 1% Cu-3.5% Ni steel (Fig. 1), which also showed significantly lower hardness values than the other parent metal steels. It was concluded that the actual strength of this particular plate was lower than that indicated in Table 2. Particularly for T-1 and CHT-100 parent metal steels, there was a tendency for delamination to occur along the rolling plane, giving the fracture faces a layered appearance (Fig. 2). Weld metal fracture faces were usually rougher than parent metal faces (Fig. 3).

Using the stereomicroscope to examine all fracture surfaces, parent metal specimens broken in 3.5% NaCl solution while coupled to zinc did not exhibit a readily visible zone of EC adjacent to the fatigue pre-crack. However, weld metal specimens broken under the same conditions showed a distinctive roughened zone 2 to 5 mm (0.08 to 0.2 in.) wide adjacent to the smooth pre-crack. Within this zone, assumed to represent EC of the hydrogen embrittlement variety, there were many small facets capable of reflecting a beam of incident light.

For T-1 steel specimens fractured under c.p., the scanning electron microscope (SEM) was used to examine fracture faces of weld and parent metal. In both cases, evidence of environmentally induced brittle cracking mechanisms was observed in the zone adjacent to the fatigue pre-crack (Fig. 4). It was assumed that corresponding areas of fracture faces of the other two alloys would show similar features if examined using the SEM.

#### DISCUSSION

As noted previously, the hardness values measured on 1% Cu-3.5% Ni parent metal 25-mm (1-in.) plate did not conform to the yield and tensile strength data supplied. The EC results as a whole were therefore more appropriately assessed with respect to hardness values and approximate tensile strengths. This is shown in Fig. 5, where the  $K_{Ii}$  (c.p.)/ $K_{Ii}$  (dry) ratios are plotted versus

Rc hardness values. To add some perspective, hitherto unreported results are included which were obtained in similar EC tests on a parent metal pipeline steel. This steel, designated F, had a yield strength of 449 MPa (65 ksi). Reference 7 may be consulted for additional information. In environments where catalyst poisons favouring hydrogen embrittlement (such as H<sub>2</sub>S) are absent, pipeline experience has shown that steels at the yield strength level of steel F are immune from external EC caused by cathodic protection systems[8].

On the basis of Fig. 5, the off-standard parent metal plate of 1% Cu-3.5% Ni steel with an approximate tensile strength of about 735 MPa (107 ksi) would also be expected to be immune to this variety of EC. The behaviour of the parent metal steels with approximate tensile strengths in the range of 830 to 970 MPa (120 to 135 ksi) is less predictable. Degradation of load-carrying capability because of hydrogen embrittlement was certainly significant, particularly for the weld metal specimens.

Available information from the Canadian Armed Forces indicates that current applications of the steels under discussion involve lengthy exposures to marine atmosphere with periods of intermittent wetting by sea water. Inorganic zinc coatings are used for corrosion protection. To date, no failures by EC have been reported. It should be taken into consideration, however, that these steels might show EC damage under a particularly unfavourable combination of circumstances, particularly in or near welds. In the present work, weld heat-affected zone (HAZ) characteristics were not studied, but research at PMRL on welded line-pipe steels suggests that the HAZ may be the region most susceptible to EC[7,9].

Confirming this, DND have reported intergranular EC in the HAZ of a butt weld on a structure of T-1 steel subsequent to a double pickling in H<sub>2</sub>SO<sub>4</sub> + HCl + corrosion inhibitor. The pickling was performed preparatory to galvanizing[10].

It is recommended that before these high-alloy steels are used in applications of greater severity with respect to hydrogen embrittlement, realistic field tests on model assemblies incorporating all the principal design and anti-corrosion features should be carried out[11]. Appropriate laboratory tests should also be carried out.

#### SUMMARY

1. Rising-load cantilever EC tests were performed on notched, fatigue pre-cracked specimens of three high-strength alloy steels (T-1, CHT-100, 1% Cu-3.5% Ni) with yield strengths of approximately 690 MPa (100 ksi). Both parent and weld metal were investigated.
2. Under f.c. conditions in 3.5% NaCl solution, parent metal specimens of the three steels showed little or no evidence of EC.
3. When coupled to zinc in 3.5% NaCl, the steels showed significant EC of the hydrogen embrittlement variety. Weld metal was in general more susceptible than parent metal and also more variable in its behaviour.

#### RECOMMENDATIONS

1. When used in highly corrosive marine service, these and similar high-strength alloy steels should be monitored periodically for evidence of EC, particularly in and near welds.
2. Prior to using these steels in severe hydrogen-embrittling conditions, realistic field tests and suitable laboratory investigations should be performed.

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Table 1. Chemical composition of steels, weight per cent

	T-1*	CHT-100*	1 Cu-3.5 Ni**
Carbon	0.10-0.20	0.10-0.20	0.13
Manganese	0.60-1.00	1.10-1.50	0.73
Phosphorus	0.04 max	0.03 max	0.013
Sulphur	0.05 max	0.04 max	0.022
Silicon	0.15-0.35	0.15-0.35	0.275
Molybdenum	0.40-0.60	0.20-0.30	-
Boron	0.002-0.006	0.0005-0.005	-
Nickel	0.70-1.00	-	3.83
Chromium	0.40-0.80	-	-
Vanadium	0.03-0.10	-	-
Copper	0.15-0.50	-	1.08

\*Information from Manufacturer's Data Sheets

\*\*PMRL Analysis

Table 2. Mechanical properties of steels

	<u>T-1*</u>	<u>CHT-100*</u>	<u>1 Cu-3.5 Ni**</u>
Ultimate Tensile Strength, MPa	793-931 (115-135 ksi)	793 min (115 ksi min)	839 (121.75 ksi)
Yield Strength, MPa	690 min (100 ksi min)	690 min (100 ksi min)	760 (110.25 ksi)
Elongation, %	18	18	23.6
Reduction in Area, %	50	50	65
Hardness, Rc***			
12.5 mm (1/2 in.) plate	30 (28.5-31)	24	26.5
25 mm (1 in.) plate	26.5 (22.5-30)	24 (20.5-26)	18 (14-22.5)
Weld metal	27.5 (23-31.5)	29 (22-34)	28 (20-34)

\*Information from Manufacturer's data sheets

\*\*Information supplied by Foundry Section, PMRL (based on typical plate)

\*\*\*Measured by the Corrosion Section, PMRL

Table 3. Results of rising-load cantilever tests on T-1 steel

Steel	Plate Thickness,		Environment	Specimen No.	K <sub>Ii</sub> at fracture		Approx Ratio	
							K <sub>Ii</sub> (f.c.)	K <sub>Ii</sub> (c.p.)
	mm	in.			MPa√m	ksi√in.	K <sub>Ii</sub> (dry)	K <sub>Ii</sub> (dry)
T-1 parent	12.5	0.5	dry	1	107.0	97.3	-	-
				2	104.5	95.0	-	-
			free corrosion	3	104.5	95.0	0.99	-
				4	100.4	91.3	0.95	-
			zinc-coupled	5	82.5	75.0	-	0.78
				6	84.0	76.4	-	0.79
T-1 parent	25	1	dry	7	107.4	97.6	-	-
				8	102.6	93.3	-	-
			zinc-coupled	9	82.1	74.6	-	0.78
				10	84.7	77.0	-	0.81
T-1 weld	25	1	dry	11	119.4	108.5	-	-
				12	126.5	115.0	-	-
			zinc-coupled	13	78.9	71.7	-	0.64
				14	88	81.0	-	0.72

Table 4. Results of rising load cantilever tests on CHT-100 steel

Steel	Plate Thickness,		Environment	Specimen No.	K <sub>Ii</sub> at fracture		Approx Ratio	
							K <sub>Ii</sub> (f.c.)	K <sub>Ii</sub> (c.p.)
	mm	in.			MPa√m	ksi√in.	K <sub>Ii</sub> (dry)	K <sub>Ii</sub> (dry)
CHT-100 parent	12.5	0.5	dry	1	102.5	93.2	-	-
				2	100.1	91.0	-	-
			free corrosion	3	91.1	82.8	0.90	-
				4	96.5	87.7	0.95	-
			zinc-coupled	5	83.9	76.3	-	0.83
				6	83.1	75.1	-	0.82
CHT-100 parent	25	1	dry	7	109.9	99.9	-	-
				8	111.0	100.9	-	-
			zinc-coupled	9	81.0	73.6	-	0.73
				10	81.1	73.7	-	0.73
CHT-100 weld	25	1	dry	11	121.4	110.4	-	-
				12	111.7	101.5	-	-
			zinc-coupled	13	61.8	56.2	-	0.53
				14	83.5	75.9	-	0.72
				15	51.7	47.0	-	0.44

Table 5. Results of rising load cantilever tests on 1 Cu-3.5 Ni steel

Steel	Plate Thickness,		Environment	Specimen No.	K <sub>Ii</sub> at Fracture,		Approx Ratio	
	mm	in.			MPa√m	ksi√in.	K <sub>Ii</sub> (f.c.)	K <sub>Ii</sub> (c.p.)
							K <sub>Ii</sub> (dry)	K <sub>Ii</sub> (dry)
1 Cu-3.5 Ni parent	12.5	0.5	dry	1	108.1	98.3	-	-
				2	100.5	91.4	-	-
			free corrosion	3	101.1	91.9	0.97	-
				4	92.1	83.7	0.88	-
			zinc-coupled	5	87.8	79.8	-	0.84
				6	80.2	72.9	-	0.77
1 Cu-3.5 Ni parent	25	1	dry	7	106.4	96.7	-	-
				8	103.7	94.3	-	-
			zinc-coupled	9	101.3	92.1	-	0.96
				10	101.2	92.0	-	0.96
1 Cu-3.5 Ni weld	25	1	dry	11	141.5	128.6	-	-
				12	140.1	127.4	-	-
			zinc-coupled	13	136.4	124.0	-	0.97
				14	96.0	87.3	-	0.68
				15	118.4	107.6	-	0.84

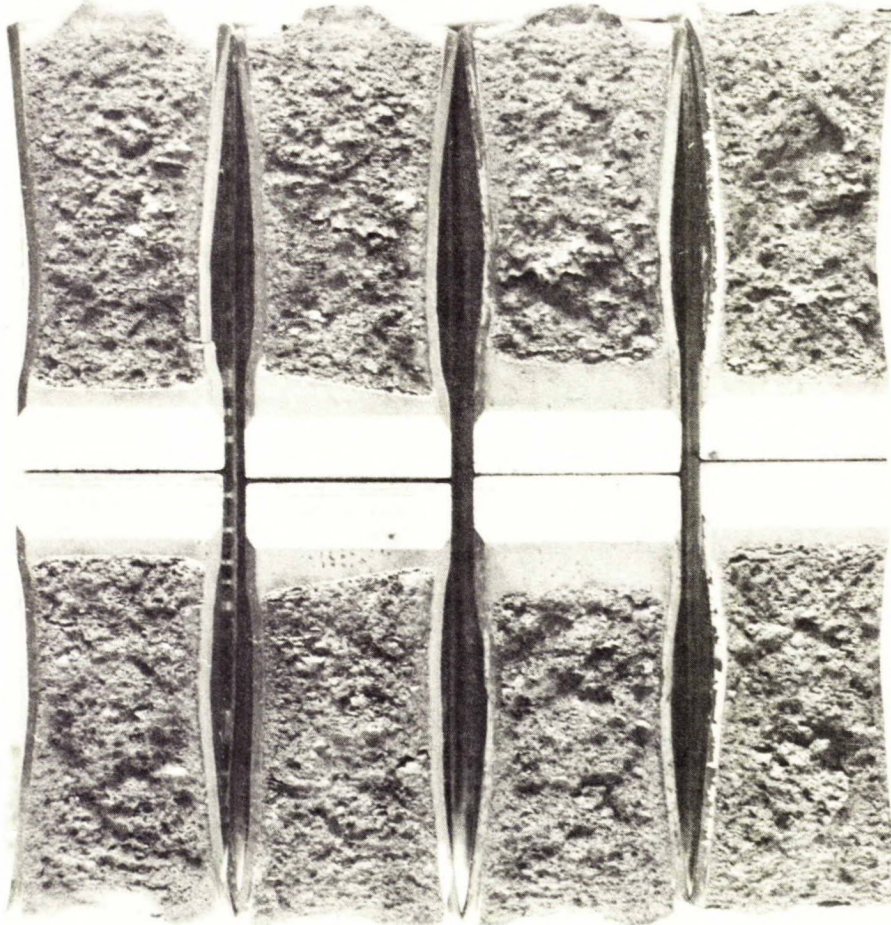


Fig. 1. Fracture faces of 1% Cu-3.5% Ni parent metal specimens from 25 mm (1 in.) plate; from left to right, specimens 7, 8, 9 and 10. (Approx X3)



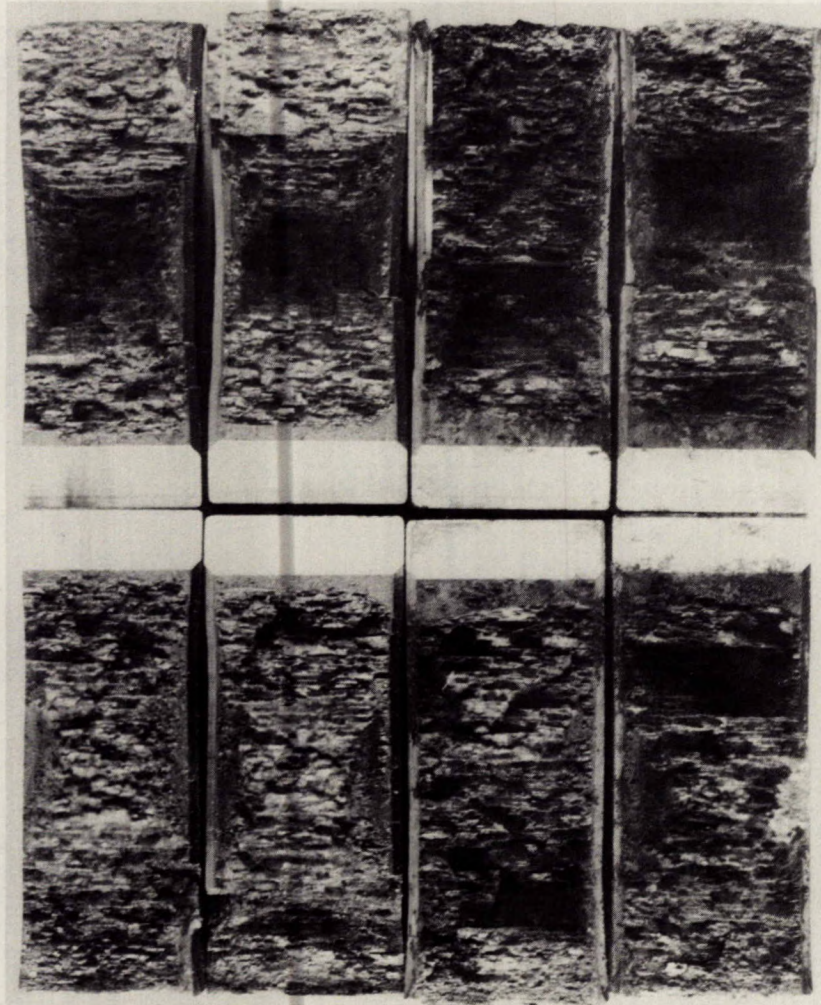


Fig. 2. Fracture faces of T-1 parent metal specimens from 25 mm (1 in.) plate; from left to right, specimens 7, 8, 9 and 10. (Approx X3)



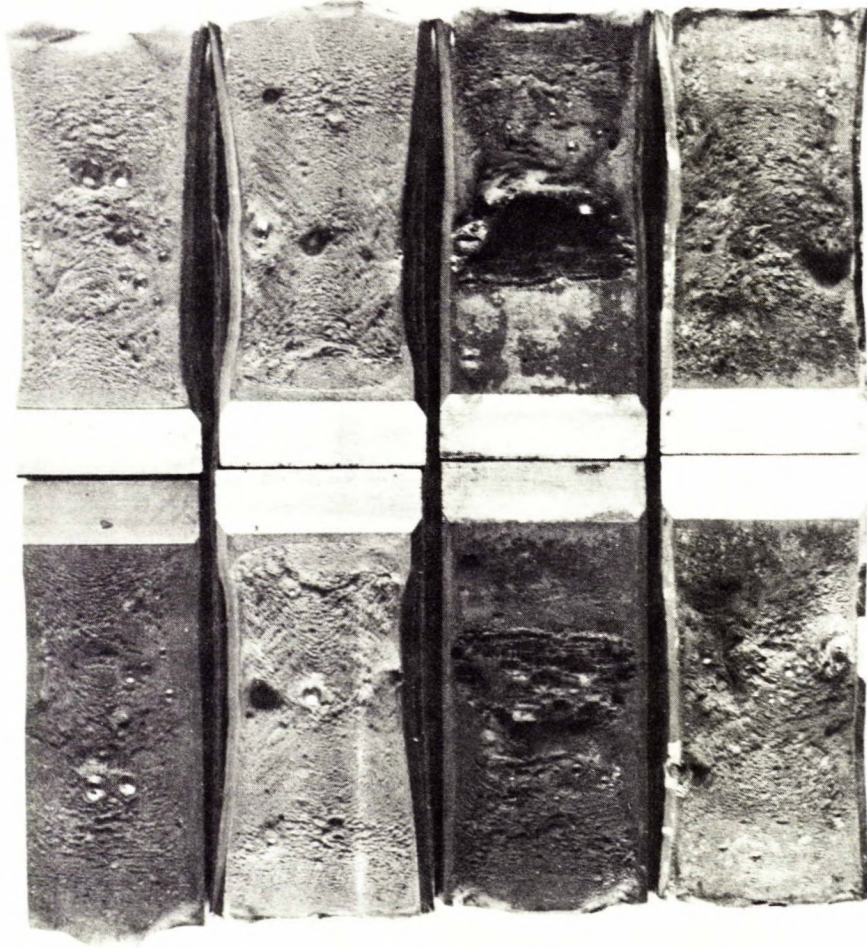


Fig. 3. Fracture faces of T-1 weld metal specimens from 25 mm (1 in.) plate; from left to right, specimens 11, 12, 13 and 14. (Approx X3)



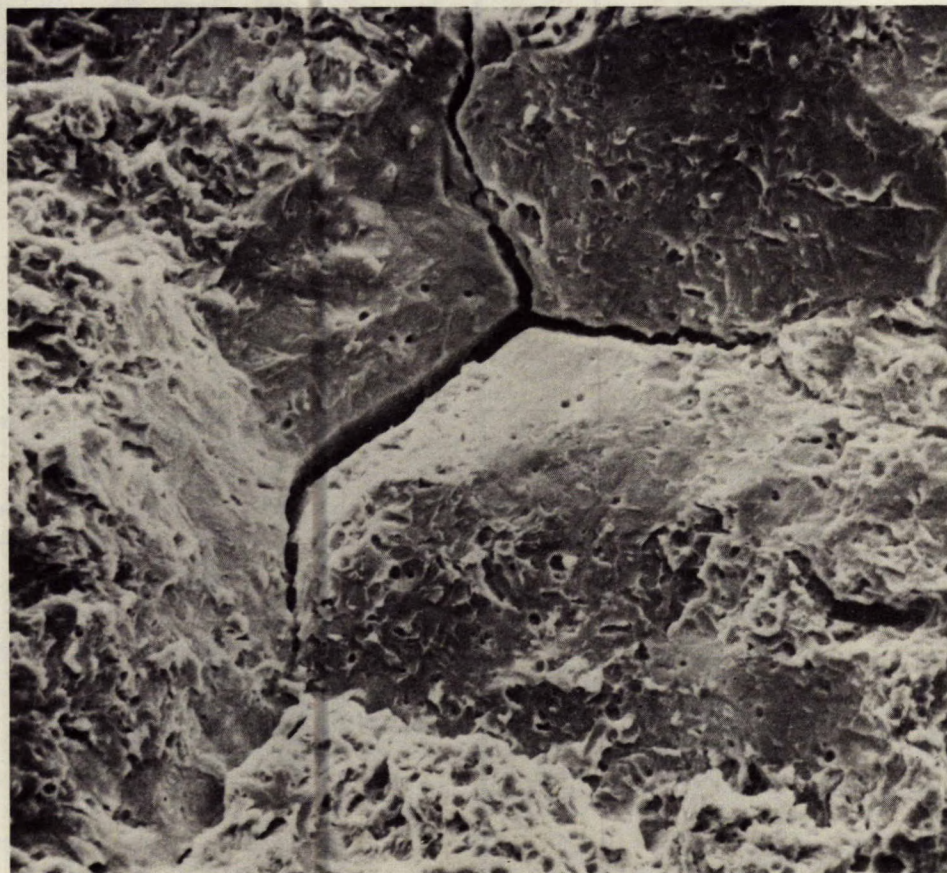


Fig. 4. Scanning electron microscope photograph of part of the environmental cracking zone of T-1 weld specimen 14 showing intergranular cracking. (X1100)

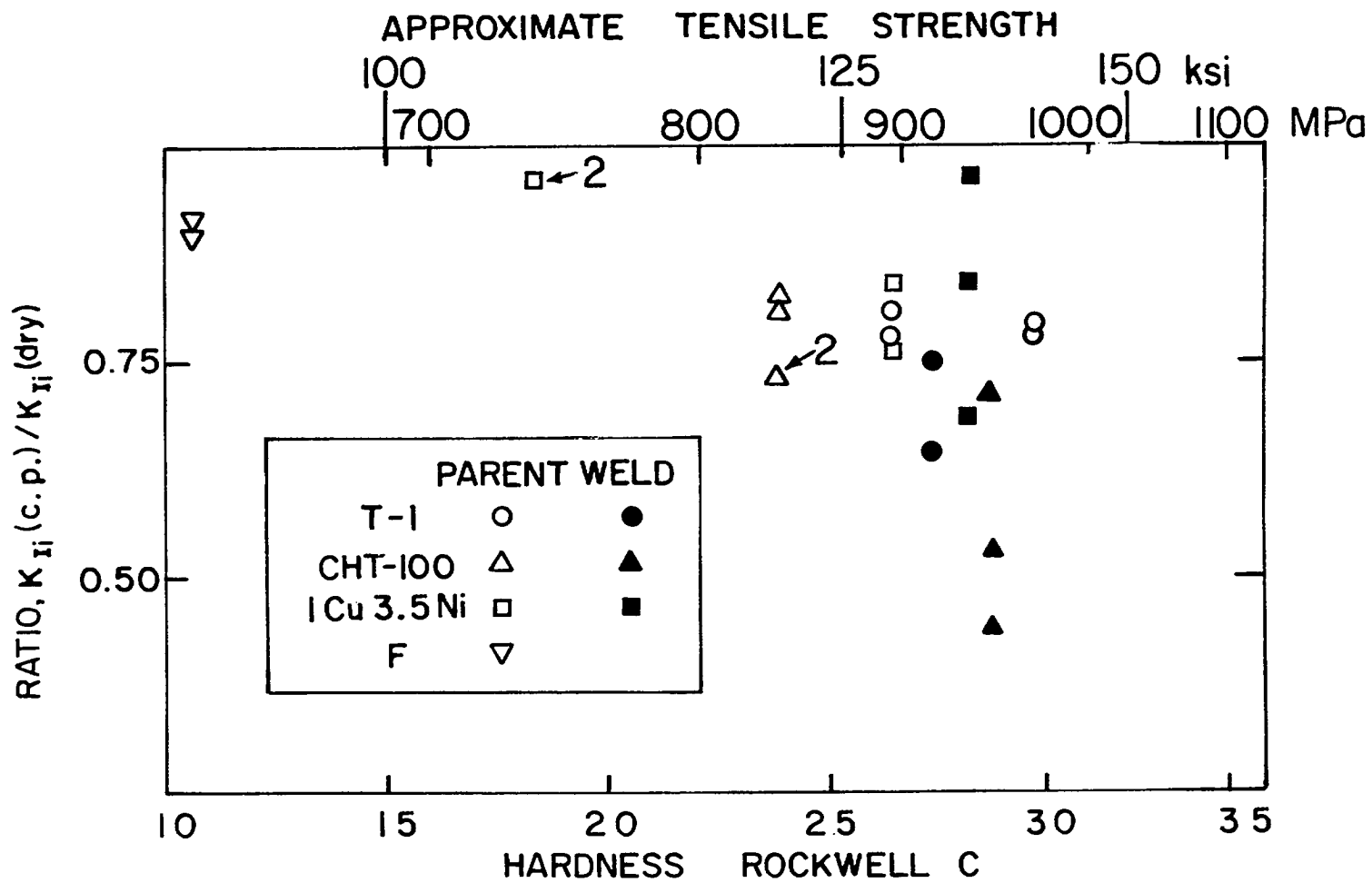


Fig. 5. Results of EC tests in 3.5% NaCl solution on specimens coupled to zinc.

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