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COLD ROLLED HIGH-STRENGTH STEEL TUBING WITH GOOD RESISTANCE TO SULPHIDE STRESS CRACKING

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Data and processes in this report represent state of art at time of publishing.

In this Technical Report there is used the following Company names and trade marks that no longer is used by Ovako AB

SKF Steel; This company name is no longer used. The organization is now part of Ovako AB.

SKF 280; This grade name is no longer in use, current versions of this grade see Ovako 280.

Technical Report 6/1983

Cold Rolled High-Strength Steel Tubing with Good Resistance to Sulphide Stress Cracking

SKF 280 — A High-Strength Low-Alloy Steel Resistant to Hydrogen-Induced Cracking in wet H_2S

Jan Tiberg, SKF Steel
Lena Hagström, Swedish Institute for Metal Research

SKF Steel

Cold Rolled High-Strength Steel Tubing with Good Resistance to Sulphide Stress Cracking

Abstract

Cold worked low-alloy steel has previously been considered to have very low resistance to sulphide stress cracking (SSC). This investigation of cold rolled, annealed tubes of grade SKF 280 shows this steel to be unsusceptible to SSC. Moreover, it is stronger than any other low-alloy steel or martensitic stainless steel with equal resistance to SSC. The tests were performed on bent-beam specimens in NACE solution. In cold rolled, annealed condition, the steel is even more resistant to SSC than the same steel quenched and tempered to the same yield strength.

Introduction

In the past few years, oil and gas exploration has started in wells that were previously considered to be impossible or very difficult to explore. Depths of more than 4600 m (15 000 ft), high pressures and aggressive environments are difficulties that must be overcome. This has led to the need for high-strength steel tubing that is resistant to H_2S sulphide stress cracking (SSC).

The resistance to SSC generally decreases with increasing strength of the steel (1—5). A continuous decrease is sometimes reported (2, 4) while an optimum is indicated in other cases, with the highest resistance to SSC stated to occur at about R_m = 800 MPa (115 ksi) or R_{eL} = 650 MPa (95 ksi) (3). Quenched and tempered steels with martensitic structures, tempered at high temperatures, are generally considered to be the low-alloy steel variants that are most resistant to SSC, and they are often specified in deep, sour wells (1, 6—9). There are also indications that cold working adversely affects SSC, and cold worked low-alloy steels are therefore generally not allowed in high strength applications in sour gas environments (7—10).

However, cold rolled, annealed, high-strength low-alloy (HSLA) steels offer great advantages as compared to quenched and tempered steels as regards strength, machinability, dimensional tolerances and surface finish, i.e. properties that are of great importance to users of tube products (11). It was therefore considered imperative to investigate the resistance to SSC of this type of steel, in spite of earlier investigations which indicate that these steels are not well suited for use in H_2S environments.

Material

A heat of grade SKF 280 steel — a high-strength low-alloy (HSLA) steel — was produced by the SKF MR process. The composition is given in *Table 1*.

The steel was hot rolled into tubes which were later cold rolled to 50.5 mm OD×34.0 mm ID (2.0×1.3 in) tube. This tube lot was separated into two batches, one of which was annealed and the other quenched and tempered. Both treatments aimed at achieving the same strength.

Heat treatment

The heat treatment conditions and the corresponding mechanical properties are given in *Table 2*.

Structure

Grade SKF 280 has a ferritic/pearlitic structure. When cold rolled and annealed, a distinct substructure develops, with low dislocation densities within the subgrains (*Fig. 1*). This structure can be expected to have good resistance to SSC.

Experimental procedure

The sensitivity to SSC was studied by the three-point bent-beam test at constant strain. The test rig is shown in *Fig. 2*. The specimens were 6 mm (0.24 in) wide, 110 mm (4.3 in) long and 2 mm (0.08 in) thick. The longitudinal axis was parallel to the longitudinal axis of the tubes. The specimens were insulated from the metallic parts of the test rig by alumina tips.

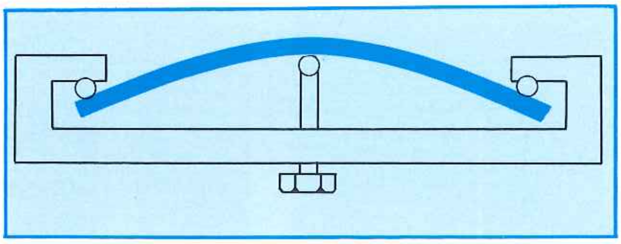

Fig. 2. Bent-beam specimen.

The specimens were strained to a number of different stresses and immersed in BP solution or in NACE solution (13) *(Table 3)*.

100 kV
Magnification 24300 times

Fig. 1. Transmission electron micrograph of the ferrite matrix of cold rolled and annealed grade SKF 280. The dislocations have largely rearranged themselves into subgrain boundaries, with low dislocation densities within the subgrains. Subgrain size: 0.2—0.5 µm (8—20 µin).

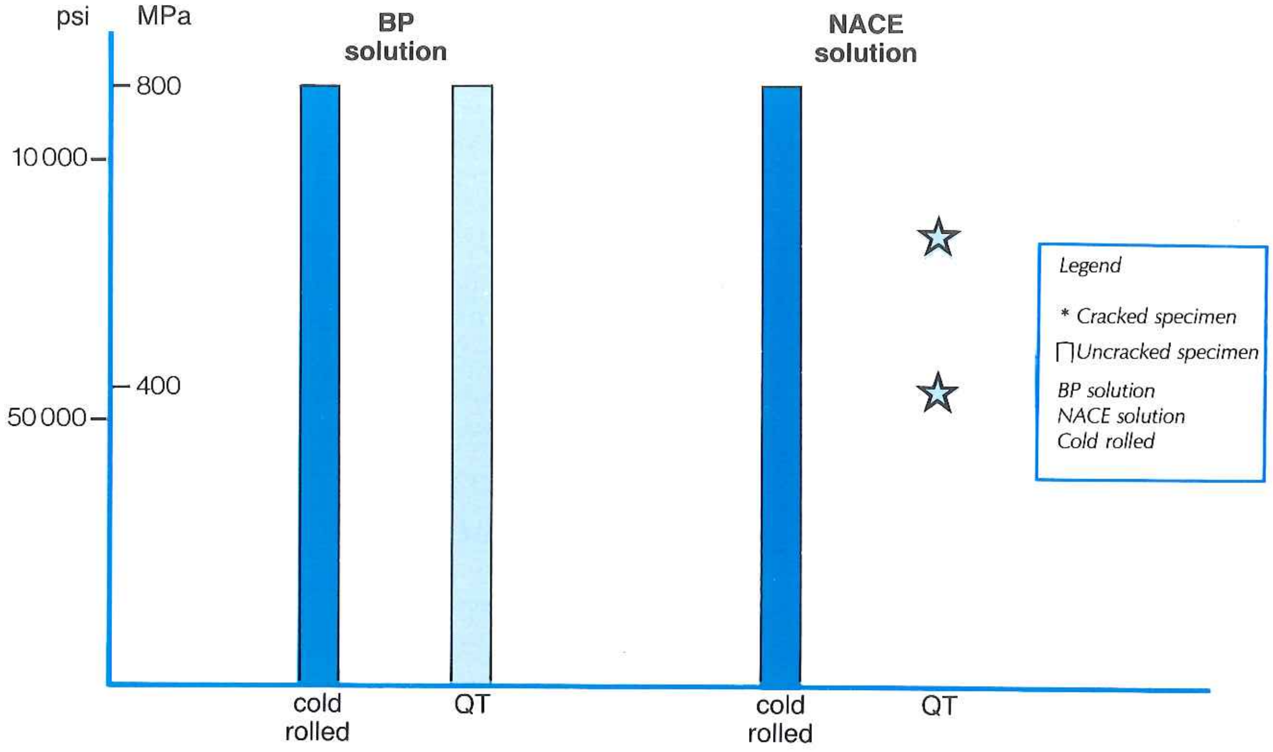

Fig. 3. *3-point bend test on grade SKF 280 cold rolled, annealed (CR+A) and quenched and tempered (QT) in BP and NACE solutions.*

Table 1. Chemical composition

C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V	Al	N
0.18	0.37	1.46	0.014	0.020	0.07	0.06	0.02	0.14	0.10	0.020	0.010

Table 2. Heat treatment and mechanical properties

	R_{eL}		R_m		A_5	Z	HB
	(MPa)	(ksi)	(MPa)	(ksi)	%	%	
1 CR+A	839	122	908	132	19	58	269
2 Q+T	866	126	906	131	19	64	300

1. Cold rolled+annealed
2. Quenched from 900°C (1650°F) in water+ tempered for two hours at 575°C (1070°F).

Table 3. Environmental test conditions

	NaCl	H_2S	HAc	pH
BP solution*	2.5%	Saturated		5.0—5.4
NACE solution (13)	5 %	Saturated	0.5%	3.0—3.8
Pressure	Atmospheric			
Temperature	Room			

* BP solution = artificial sea-water according to (12), saturated with H_2S

Results

The results are given in *Fig. 3.* In artificial sea-water, cold rolled as well as quenched and tempered steels have good resistance to SSC. Both were capable of withstanding 800 MPa (116 ksi). However, in NACE solution, the quenched and tempered steel cracked already at 400 MPa (58 ksi) (no tests were carried out at lower stresses), whereas the cold-rolled steel did not fail even at 800 MPa (116 ksi).

Comments

The good resistance of the cold rolled, annealed tubes has not previously been reported. It is notable that the resistance to SSC of the cold rolled annealed tubes is much better than that of the quenched and tempered structure of the same tubes. The occurrence of a distinct subgrain structure is a probable explanation for this behaviour.

Among the low-alloy steels and martensitic stainless steels that are not susceptible to SSC in the bent-beam test in NACE solution, cold rolled and annealed SKF 280 is the strongest ever reported in the literature (1—3, 5).

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SKF 280 — A High-Strength Low-Alloy Steel Resistant to Hydrogen-Induced Cracking in wet H_2S

Abstracts

Hydrogen-induced cracking (HIC) causes many failures in the oil and gas industry. HIC appears in sour environments in the presence of H_2S. Grade SKF 280 is a high-strength low-alloy (HSLA) steel which has been found to have an outstandingly good resistance to HIC, not only in a standard BP solution, but also in the more aggressive NACE solution. The reasons for this good resistance to HIC are the absence of glassy silicate and pancake-like sulphide inclusions in grade SKF 280 and the absence of a banded pearlite-ferrite structure.

Introduction

Wet H_2S causes many failures in steel components in the oil and gas industries. Sulphide stress cracking (SSC) has been a major problem in steel with yield strengths of 550 MPa (80 ksi) and above, and this has been discussed elsewhere (1, 2). Hydrogen-induced cracking (HIC) is a problem occurring mainly in steels with yield strengths below 550 MPa (80 ksi). Blistering or stepwise cracking are other names for the phenomenon illustrated in *Fig. 1*.

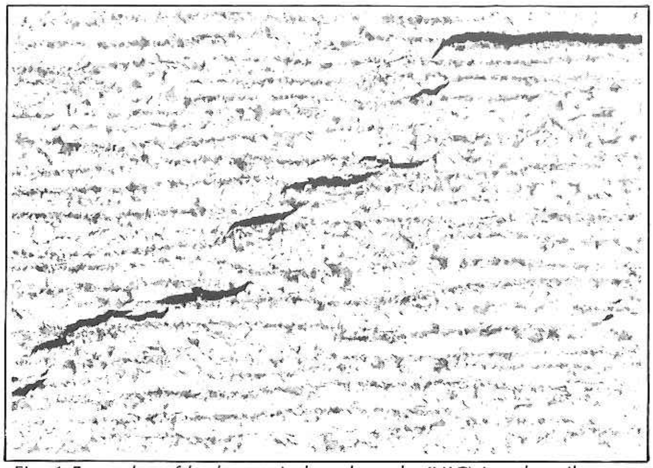


Fig. 1 Examples of hydrogen-induced cracks (HIC) in a heavily banded structure.

Hydrogen-induced cracks develop along the banding in the microstructure or along elongated non-metallic inclusions. Hydrogen recombining at high pressure in microvoids at such inhomogenieties induces stresses that initiate cracks along phase boundaries and forces the cracks to propagate.

This investigation has been performed in order to study the influence of some important material properties on HIC in some high-strength low-alloy (HSLA) steels, i.e.:

- sulphur content
- degree of banding of the structure
- inclusion morphology

Materials

Test materials were delivered by three Scandinavian steel manufacturers, one of them being SKF Steel which supplied tubes of grade SKF 280. The composition, heat treatment and mechanical properties of the various materials are given in *Table 1.*

The degree of banding was varied in three ways. The banding was increased by a higher degree of reduction on hot rolling — 30 mm (1.2 in) and 12 mm (0.5 in) plates, rolled from 175 mm (6.9 in) continuously cast slabs, were studied. In addition, tubes with wall thicknesses of 30 mm (1.2 in) and 10 mm (0.4 in) were studied. Normalizing also gave a higher degree of banding than that in the hot rolled products. Tubes and plate also have distinct differences in banding, as discussed below.

Experimental procedure

The susceptibility to HIC was tested according to the BP test method (3—6). Specimens of 20×100 mm (0.79×3.9 in), with the axis in the direction of rolling, were immersed in artificial sea-water saturated with H_2S (*Table 2*). The grade SKF 280 specimens, which had a much higher resistance to HIC, were also tested in the much more aggressive NACE solution (*Table 2*), in order to determine whether the high resistance to HIC was caused

Sample	Plate thick-ness	Heat treatment	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V	Al	Nb	N	R_{eL}	R_m	A_5
A 47	30 mm	normalized	.15	.43	1.42	.025	.001	.07	.02	.02	.01	.01	.042	.027	.005	⩾350MPa	⩾510MPa	⩾22%
A 43	,,	,,	.17	.39	1.43	.019	.013	.03	.02	.01	.01	.01	.026	.025	.010	,,	,,	,,
A 44	,,	,,	.15	.45	1.52	.019	.025	.02	.01	.01	.01	.01	.036	.025	.006	,,	,,	,,
A 71	12 mm	Q.T.	.15	.41	1.32	.023	.001	.06	.02	.00	.02	.01	.027	.021	.004	520	636	22
A 70	,,	,,	.15	.43	1.42	.020	.018	.02	.02	.01	.02	.01	.021	.025	.008	550	654	17
A 46	,,	,,	.16	.41	1.39	.020	.025	.01	.01	.00	.01	.01	.021	.025	.006	560	668	15
A 73	12 mm	normalized	.15	.41	1.32	.023	.001	.06	.02	.00	.02	.01	.027	.021	.004	⩾350	⩾510	⩾22
A 75	,,	,,	.16	.42	1.33	.024	.003	.06	.02	.00	.01	.01	.024	.020	.004	,,	,,	,,
A 72	,,	,,	.15	.43	1.42	.020	.018	.02	.02	.01	.02	.01	.021	.025	.008	,,	,,	,,
A 45	,,	,,	.16	.41	1.39	.020	.025	.01	.01	.00	.01	.01	.021	.025	.006	,,	,,	,,
B 1	20 mm	Control	.17	.36	1.53	.011	.005	.04	.01	.01	.03	–	.054	–	.008	380	543	34
B 2	,,	rolled	.16	.40	1.58	.024	.027	.06	.04	.01	.09	–	.049	–	–	430	578	32
	SKF 280 Tube wall																	
1	10	asrolled	.19	.36	1.49	.009	.013	.08	.08	.03	.24	.09	.033	–	–	540	720	24
2	10	normalized	.19	.36	1.49	.009	.013	.08	.08	.03	.24	.09	.033	–	–	480	630	30
3	10	asrolled	.16	.36	1.44	.012	.026	.12	.10	.03	.22	.08	.031	–	–	500	680	23
4	10	normalized	.16	.36	1.44	.012	.026	.12	.10	.03	.22	.08	.031	–	–	470	610	30
5	30	asrolled	.18	.35	1.42	.008	.012	.16	.08	.02	.16	.08	.022	–	–	470	650	24
6	30	normalized	.18	.35	1.42	.008	.012	.16	.08	.02	.16	.08	.022	–	–	420	580	30
7	30	asrolled	.16	.33	1.41	.010	.027	.19	.11	.08	.22	.07	.024	–	–	470	650	24
8	30	normalized	.16	.33	1.41	.010	.027	.19	.11	.08	.22	.07	.024	–	–	430	590	30

Table 1. Chemical composition, heat treatment and mechanical properties.

by the high copper content. Copper has been shown to reduce the HIC sensitivity in solutions with a pH of 4 or above, i.e. in the BP solution but not in the NACE solution (8).

Table 2. Compositions of test solutions

	NaCl	H_2S	HAc	pH
BP solution*	2.5%	Saturated		5.0—5.4
NACE solution (9)	5 %	Saturated	0.5%	3.0—3.8
Pressure	Atmospheric			
Temperature	Room			

* BP solution = artificial sea-water according to (7), saturated with H_2S

After the immersion, the content of hydrogen was measured according to the gluzerine method (3) and the samples were sectioned longitudinally. The relative crack lengths were measured according to (3, 4, 6) as shown in *Fig. 2.*

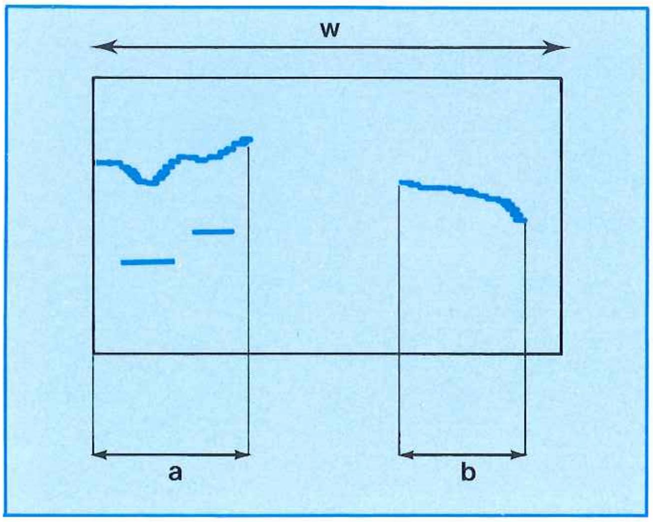


Fig. 2. Crack length ratio (CLR)

$$CLR = \frac{a+b}{w}$$

i.e. projected length of cracks relative to width of sample.

Results

The results are summarized in *Fig. 3—5.* The following conclusions can be drawn from these graphs:

- There is a clear correlation between crack length ratio (CLR) and hydrogen pick-up (*Fig. 5*). This is expected in hydrogen-induced cracking (HIC).
- HIC is sensitive to the sulphur content of the steel. The higher the sulphur content, the higher the hydrogen pick-up and the higher the CLR (*Fig. 3—4*).
- The thinner section of 12 mm (0.47 in) had a higher HIC sensitivity than the thick sections (*Fig. 3—4*).
- Quenched and tempered structures display less HIC sensitivity than the same steel plates in the normalized condition (*Fig. 3—4*).
- Heavy pearlite banding increases the HIC (*Fig. 1 and 4*).
- At the same sulphur level, grade SKF 280 exhibited a much lower HIC sensitivity than any of the other steel grades tested. The CLR was nil in all grade SKF 280 samples tested in BP solution, except for a very small crack in one of the high-sulphur samples. That sample had a CLR of 0.4%, which is negligible. Even in the more aggressive NACE solution, SKF 280 was almost intensitive to HIC, as illustrated by *Table 3.*

Table 3. HIC test on SKF 280 in NACE solution

Sample	Wall thickness mm	in	Heat treatment	S content	Hydrogen pick-up ml/100 g	CLR
SKF280						
1	10	0.39	as rolled	low	4.3	0%
2	10	0.39	normalized	low	3.9	0%
3	10	0.39	as rolled	high	4.7	0%
4	10	0.39	normalized	high	4.8	6%
5	30	1.18	as rolled	low	3.5	5%
6	30	1.18	normalized	low	3.4	0%
7	30	1.18	as rolled	high	4.1	1%
8	30	1.18	normalized	high	4.1	0%

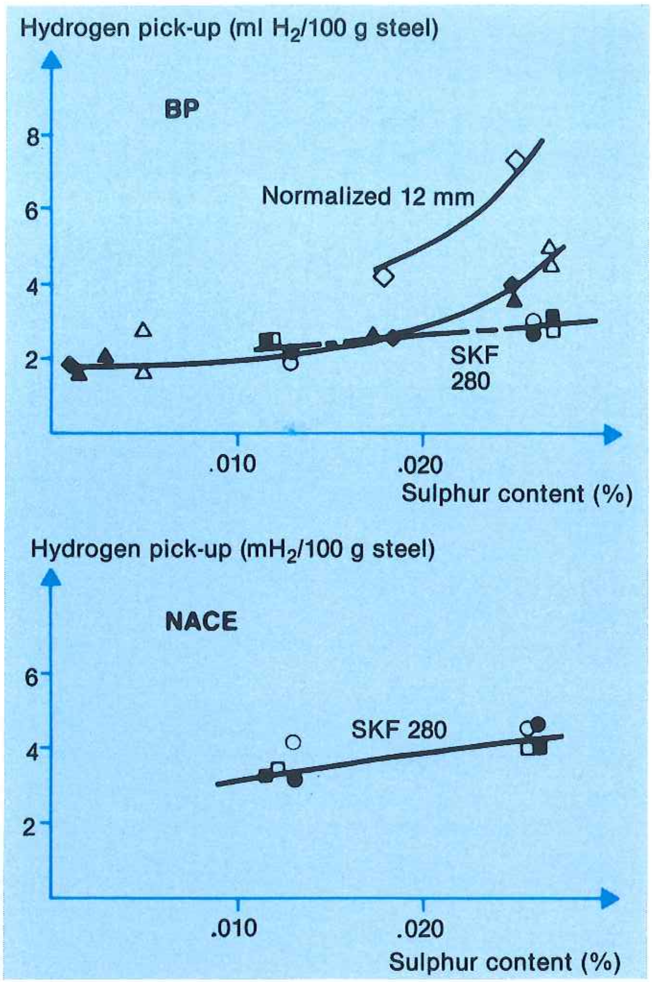


Fig 3
Hydrogen pick-up at different sulphur contents in BP or NACE solution.

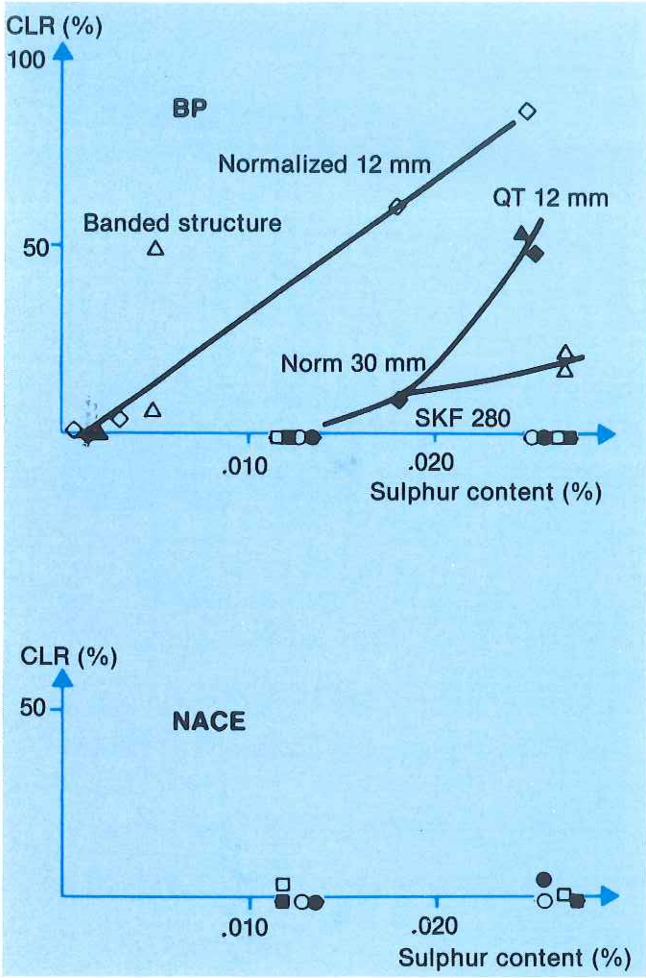


Fig 4
Crack Lenght Ratio (CLR) at different sulphur contents in BP or NACE solution.

○	Hot rolled	10	mm	wall	from	SKF
●	Normalized	,,	,,	,,	,,	,,
□	Hot rolled	30	,,	,,	,,	,,
■	Normalized	,,	,,	,,	,,	,,
◇	Normalized	12	,,	plate	,,	A
◆	Q&T	,,	,,	,,	,,	,,
▲	Normalized	30	,,	,,	,,	,,
△	Control rolled	18	,,	,,	,,	B

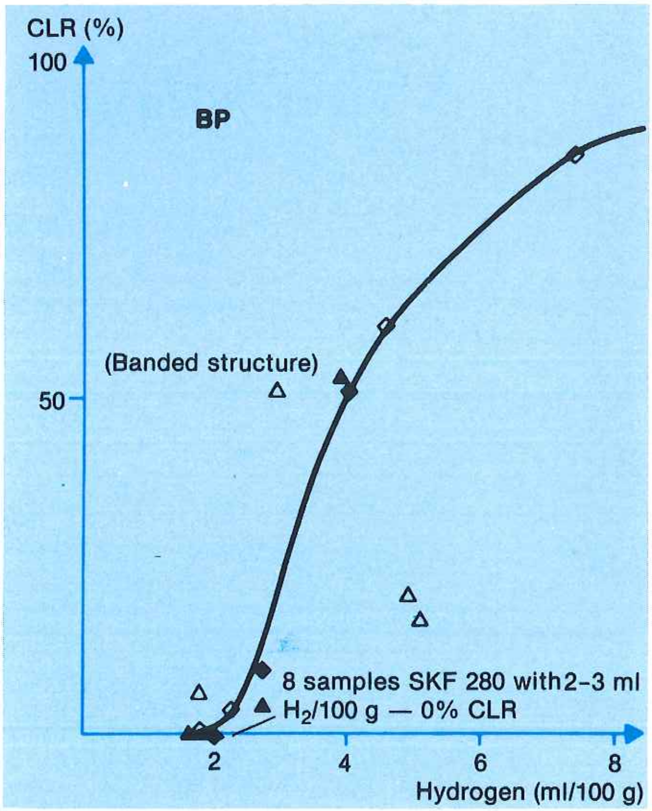
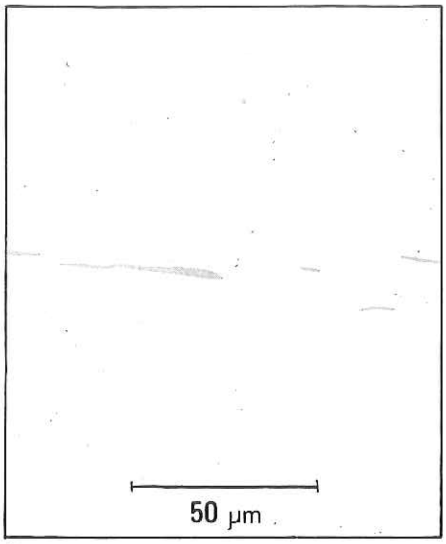
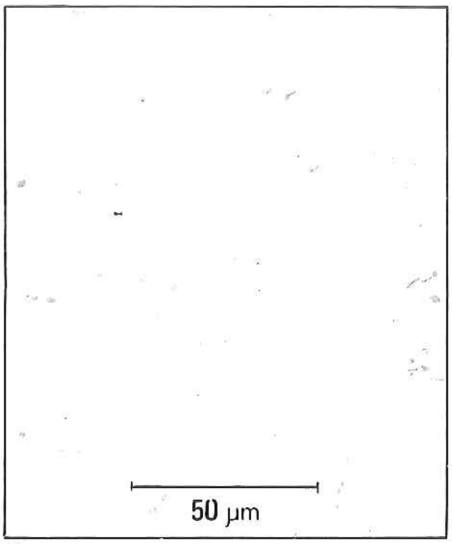


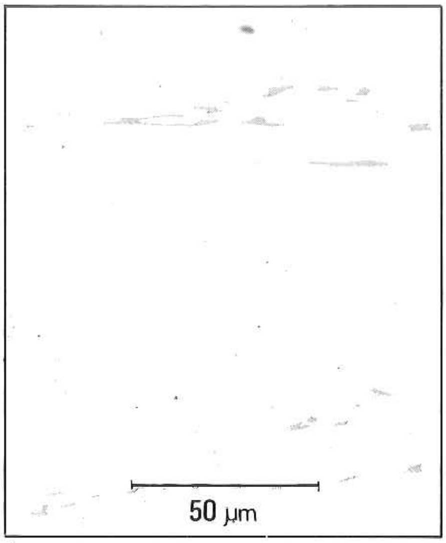
Fig 5
Relation between crack lenght ration (CLR) and hydrogen pick-up.



6a
Longitudinal section of grade SKF 280 seamless tubing, showing elongated MnS inclusions in the direction of rolling.



6b
Transverse section of grade SKF 280 seamless tubing, showing MnS inclusions of very modest size in the transverse direction.



6c
Transverse section of commercial plate, showing the spread of the MnS inclusions, which indicates their pancake shape.

Discussion

Small additions of copper and chromium to steel have been shown on several occasions to prevent HIC or to decrease the susceptibility of the steel to HIC at a pH above approx. 4 (9). Grade SKF 280 has high enough copper and chromium contents for the HIC susceptibility to be reduced considerably (7—11). Besides, the sulphides in grade SKF 280 have a morphology that reduces the HIC susceptibility. In grade SKF 280 (*Fig.* 6), the sulphides appear as stringers, whereas wide pancake-shaped sulphides are usual in the specimens taken from plates. The sulphide morphology in grade SKF 280 is probably of greater importance than the high copper and chromium contents, since grade SKF 280 had a high resistance to HIC, even in NACE solution (9). Moreover, grade SKF 280 is free from glassy silicates and massive columbium carbonitrides which have been reported to act as initiation points (11). From *Fig. 5,* it is evident that grade SKF 280 has a low CLR compared to its hydrogen pick-up. These factors make grade SKF 280 a very suitable steel for environments containing H_2S.

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SKF Steel
Technology
P.O. Box 133, S-182 12 Danderyd, Sweden
SKF

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Ovako AB
SE-111 87 Stockholm, Sweden
Phone: +46 (0)8 622 13 00

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