# SULFIDE STRESS CORROSION CRACKING IN STEELS FOR THE OIL INDUSTRY

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ABSTRACT - The following steels have been chosen for this work: API 5AC L80, AISI 4137H, AISI 420 - API 5AC C90, 22Cr-5.5Ni-3Mo, 27Cr-31Ni-3.5Mo. The tests have been performed both in NACE solution, both in modified NACE solution (in which a 90% $CO_2$ plus 10% $H_2S$ gas was bubbling). Smooth specimens (to obtain applied stress-time to failure curves) and also precracked specimens (to obtain the $K_{ISCC}$ values an the critical defect depths) have been used. The impossibility of using carbon or low alloy steels at high strength levels when relevant $H_2S$ contents are present has been confirmed. The good behaviour of smooth specimens of cold worked duplex stainless steel has been shown; but tests with fracture mechanics specimens show how these results cannot be extrapolated in conditions in which sharp defects are present.

## 1 - INTRODUCTION

One of the greatest problems that the oil industry is presently being faced with is to find a satisfactory solution for the availability of steels and their resistance in environments with high Hydrogen Sulfide contents.

As noted this type of envirorment may cause stress corrosion (SSCC = Sulfide Stress Corrosion Cracking) (1-4). This problem became evident over the last years following the necessity of exausting more and more profound deposits (7,000 - 10,000 m and more) as a result of the depletion of those less profound. This resulted in increasing the weight of the extraction line (tubing) and thus the need to use high strength steels that are more susceptable to SSCC.

Where high content of $CO_2$ is found, an other problem of an adequate resistance to general corrosion will arise (5-9). This problem can be solved with the traditional C-Mn steel using corrosion inhibitors inserted into the wells, or utilising steels with high chromium content (for example AISI 420 stainless steel).

The necessity to use steels with high mechanical resistance together with adequate resistance to general corrosion and good resistance to SSCC, has been of rising interest in the development and the use, for these applications, of high alloyed steels like 22Cr-5.5Ni-3Mo duplex stainless steel and 27Cr-31Ni-3.5Mo superaustenitic stainless steel (10-12).

The cost of duplex steel is three to six times that of a C-Mn steel (the difference is a drop of about two when the inhibition cost is considered) but this may be compensated by the reliability of these solution rendering it competitive even if it would require only one less intervention of maintenance within ten years of production.

In order to define the limits of use, diagrams plotting usability versus temperature, $CO_2$ and $H_2S$ contents have been developed for each steel (13). To realize these diagrams smooth or precracked specimens subjected to constant stress or constant deformation are normally used. As a result of some unsuccesfull use, it is advisable to study with more detail the behaviour of various steels in the presence of sharp defects.

Results of the tests that have been performed to prove the characteristic conduct of traditional and innovative steels are recorded in the present work. Also specimens containing sharp defects have been utilized (mechanical fracture type tests).

The tests have demonstrated how the resistance of steel in a given environment is not of an absolute value, but is dependent on the size of the defects present.

## 2 - TESTED MATERIALS

The following steels have been chosen for this work: a traditional, non-elevated mechanical characteristic steel, that is a C-Mn API 5AC L80; an AISI 420 martensitic stainless steel (API 5AC C90); an hardened and tempered high strength Cr-Mo steel AISI 4137H that has been used for drill-pipes; the two more promising innovated stainless steels, that is a 22Cr-5.5Ni-3Mo duplex stainless steel and a 27Cr-31Ni-3.5Mo superaustenitic stainless steel together cold worked to improve the mechanical properties.

Tabb. 1 and 2 give the chemical composition and the principal mechanical characteristics of the tested steels. Fig. 1 gives the microstructures:
- the API 5AC L80, AISI 4137H and AISI 420 (API

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Research supported by "Progetto Finalizzato Metallurgia del C.N.R.".

| STEEL | C | Mn | Si | P | S | Cr | Ni | Mo | Cu | Al | Sn | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| API 5AC L80 | 0.30 | 0.80 | 0.19 | 0.016 | 0.021 | 0.13 | 0.08 | 0.04 | 0.17 | 0.01 | 0.008 | - |
| AISI 4137H | 0.41 | 1.00 | 0.31 | 0.010 | 0.016 | 0.97 | 0.23 | 0.20 | - | - | - | - |
| AISI 420 (API 5AC C90) | 0.22 | 0.51 | 0.34 | 0.030 | 0.001 | 13.46 | 0.28 | 0.06 | - | - | - | - |
| 22Cr-5.5Ni-3Mo | 0.02 | 1.59 | 0.33 | 0.022 | 0.030 | 21.95 | 5.51 | 2.95 | - | - | - | 0.16 |
| 27Cr-31Ni-3.5Mo | 0.02 | 1.60 | 0.04 | 0.019 | 0.030 | 26.35 | 31.89 | 3.99 | 1.00 | - | - | - |

Tab. 1 - Chemical composition of the tested steels.

| STEEL | UTS (MPa) | TYS (MPa) | $HR_c$ | A (%) | $K_{IQ}$ ($MPa\sqrt{m}$) |
|---|---|---|---|---|---|
| API 5AC L80 | 776 | 622 | 21.0 | 27.6 | - |
| AISI 4137H | 1049 | 952 | 33.0 | 17.5 | 107 |
| AISI 420 (API 5AC C90) | 828 | 652 | 22.5 | 21.4 | 82 |
| 22Cr-5.5Ni-3Mo | - | 980 | 29.0 | 9.0 | 100 |
| 27Cr-31Ni-3.5Mo | - | 770 | 25.0 | 13.0 | 73 |

Tab. 2 - Mechanical properties of the tested steels.

5AC C90) steel, demonstrate a tempered martensitic structure with traces of pre-existent austenitic grains;
- the 22Cr-5.5Ni-3Mo steel demonstrates a bifasic structure, with geminates in the austenitic grains;
- the 27Cr-31Ni-3.5Mo steel presents an austenitic structure with geminates and cold deformation bands.

3 - TEST ENVIRONMENTS

Two different environments have been used to carry out the tests:
- the NACE environment (14), i.e. a solution of 5% NaCl + 0.5% $CH_3COOH$ saturated with $H_2S$ (after deaeration with $N_2$), room temperature, pH = 3.5 ÷ 3.8;
- a modified NACE environment, i.e. a solution analogous to the previous one in which a 90% $CO_2$ plus 10% $H_2S$ gas was bubbling; the pH doesn't vary with respect to NACE environment.

The NACE solution is the severest of the normally used environments in Hydrogen Sulfide tests, due to the low pH and the high NaCl and $H_2S$ (3000 ppm) contents. The second environment is closer to the actual conditions in oil wells.

4 - SPECIMENS, TEST PROOF AND RESULTS

4.1 - Smooth specimens

In order to discover the applied stress - time to failure diagrams, cylindrical specimens of total 100 mm length with 20 mm parallel length and 3 mm diameter have been used. The surfaces of the test specimens were rectified and smoothed with humide abrasive paper of 1000 mesh.

The test specimens were loaded using constant load machines in which the strength, applied with dead weights, is multiplied with a double lever arm. Elimination of the flexion component was achieved by turning the threaded extremes of the specimen that protrudes from the cell into ball joints with a nut-screw. Fig. 2 shows the ball-joints, specimen and test cell assembly.

The tests have been performed according to the following procedure:
- solution deaeration with $N_2$ for at least two hours;
- assembling of specimen, ball-joints and cell;
- admission of the solution into the cell under bubbling nitrogen;
- mounting of the test cell on the loading machine and connecting the $H_2S$ feeding tubes;
- saturation of the solution with the $H_2S$-containing-gas via bubbling for at least 30 minutes;
- application of loading and beginning of time monitoring;
- persecution of $H_2S$-containing-gas bubbling during testing time;
- recording of the failing time (via automatic time clock) or interruption of the test after 1000 hours.

The results of tests in the two solutions are shown in Fig. 3 and summarized in Fig. 4.

4.2 - Precracked specimens

The precracked specimen tests were performed using constant deformation 1/2" thick WOL -modified specimens (15), with shallow face notch for maintaining the stress corrosion crack perpendicular to the loading direction (Fig. 5).

The specimens have been fatigue-pre-

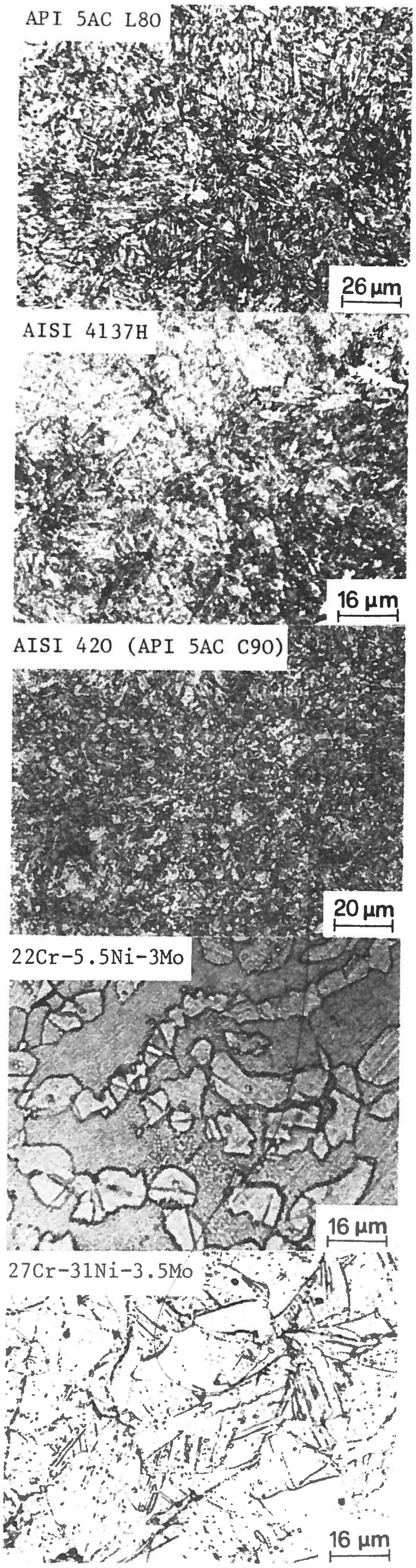



Fig. 1 - Microstructures of the tested steels.

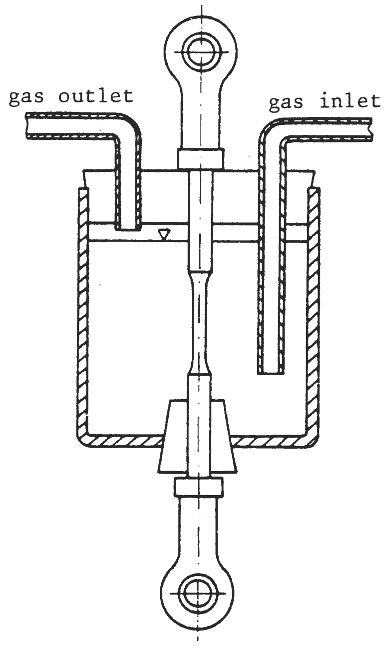



Fig. 2 - Ball-joints, specimen and test cell assembly.

cracked according to the ASTM E399 standard, loaded to different values of initial $K_I$ and introduced in NACE solution for 1000 hours.

At the end of the test the specimens were opened mechanically, after the immersion in liquid nitrogen, while the fatigue and corrosion crack lengths were measured by using the following formula:

$$a = \frac{a_{left} + 4a_{1/2} + a_{right}}{6}$$

In order to calculate the values of $K_I$ the following formula already proposed for 1" specimen (16) and verified also for 1/2" specimens with shallow face notch (17), has been used:

$$K = \frac{1 + \frac{E.B.L_b}{E_b.A_b} . Q(a_o/W)}{1 + \frac{E.B.L_b}{E_b.A_b} . Q(a/W)} .$$

$$V_o . \frac{a_o}{a_o + C} . \frac{E.B}{\sqrt{B.B_n} . a} . Q(a/W) . C_3(a/W)$$

where:

K = stress intensity factor (MPa$\sqrt{m}$);
B = specimen thickness (m);
$B_n$ = specimen thickness refering to the notch (m);
W = specimen depth measured from the loading axis (m);

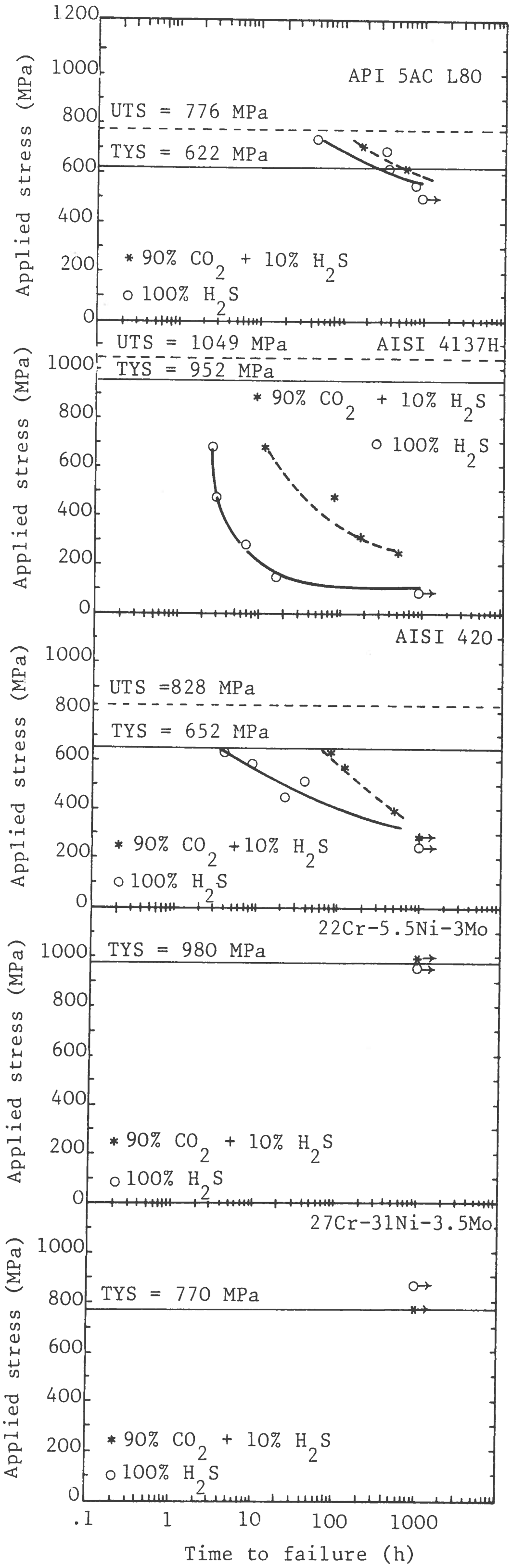



Fig. 3 - Results of the smooth specimen tests in NACE environment and in NACE-modified environment for each tested steel.

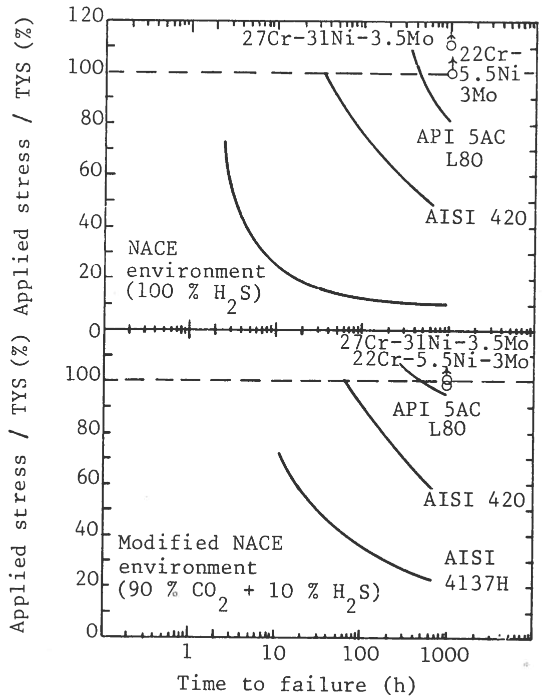



Fig. 4 - Results of the smooth specimen tests in NACE environment and in NACE-modified environment.

C = positional distance of the clip-gauge from the loading axis (m);
E = Young's modulus (MPa);
$a_o$ = fatigue crack length measured from the loading axis (m);
a = SSCC crack length measured from the loading axis (m);
$V_o$ = notch opening measured by clip-gauge (m);
$E_b$ = loading bolt Young's modulus (MPa);
$L_b$ = free length of loading bolt plus two threads (m);
$A_b$ = area of the loading bolt contact section with the pin ($m^2$);

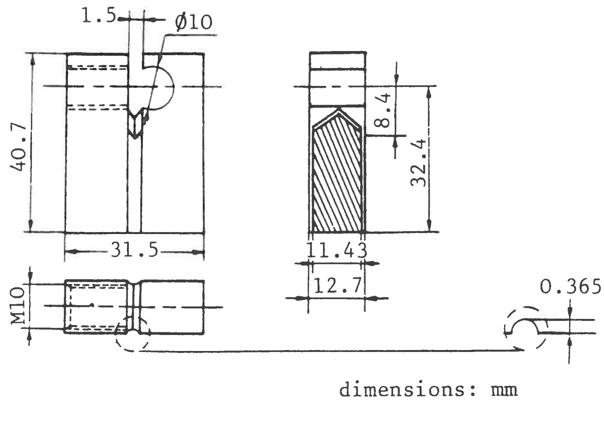



Fig. 5 - 1/2" thick WOL-modified specimen, with shallow face notch.

| STEEL | $V_o$ (mm) | $a_o$ (mm) | $K_{Iinit}$ (MPa$\sqrt{m}$) | $a_{SSCC}$ (mm) | $K_{ISSCC}$ (MPa$\sqrt{m}$) | Plain strain |
|---|---|---|---|---|---|---|
| API 5AC L80 | tests not realized for insufficient tickness of the steel | | | | | |
| AISI 4137H | 0.182 | 11.4 | 37 | 29.8 | 9 | valid |
| | 0.363 | 13.1 | 69 | 31.7 | 6 | valid |
| AISI 420 (API 5AC C90) | 0.128 | 12.0 | 26 | 12.0 | >26 | valid |
| | 0.165 | 9.4 | 37 | 9.4 | >37 | valid |
| 22Cr-5.5Ni-3Mo | 0.252 | 11.0 | 53 | 14.1 | 43 | valid |
| | 0.575 | 11.4 | 118° | 27.0 | 50 | partially |
| 27Cr-31Ni-3.5Mo | 0.302 | 11.8 | 61 | 11.8 | >61 | partially |
| | 0.852 | 13.3 | 160° | 13.3 | -°° | - |

° nominal value ($K_{Iinit} > K_{IQ}$) °° undefinible value

Tab. 3 - Results of $K_{ISSCC}$ tests.

$$Q(a/W) = 0.53753 - 1.89044(a/W) + 4.8038(a/W)^2 + - 6.45671(a/W)^3 + 4.3889(a/W)^4 - 1.1831(a/W)^5;$$

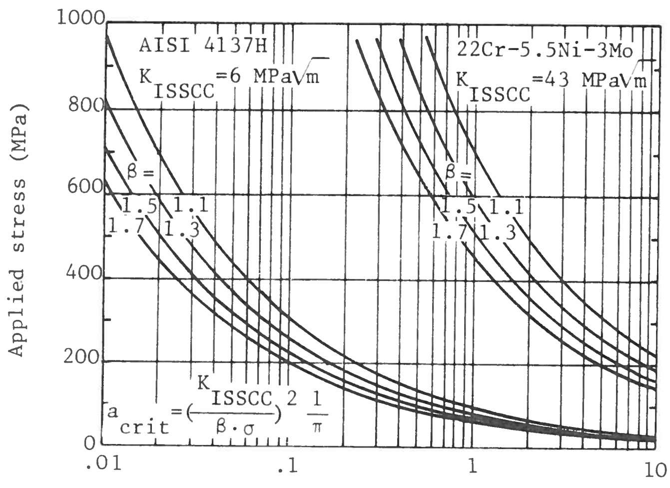
$$C_3(a/W) = 30.96(a/W) - 195.8(a/W)^2 + 730.6(a/W)^3 + - 1186.3(a/W)^4 + 754.6(a/W)^5$$

The summary of results has been given in Tab. 3.

Using the obtained $K_{ISCC}$ values it is possible to determine for each material the depth of the minimum defect size that is able to engage in the stress corrosion phenomenon. This dimension can be evaluated via the relationship

$$a = \left(\frac{K_{ISCC}}{\beta \cdot \sigma}\right)^2 \cdot \frac{1}{\pi}$$

The critical defect dimension that is able to engage in SSCC phenomenon for tested




$$\beta = 1.12 + 0.31(a/t) + 6.85(a/t)^2 - 12.12(a/t)^3 + 10.03(a/t)^4$$

Fig. 6 - Critical defects of the tested steels, as a function of nominal applied stress and of the shape factor value.

materials is plotted in Fig. 6, as a function of nominal applied stress and of the shape factor value (18).

Tab. 4 quotes for each material the depth of critical defects for a nominal stress of 70% of yield strength and a shape factor value of 1.1 (valid for less deep elliptical defects).

| STEEL | $K_{ISSCC}$ (MPa$\sqrt{m}$) | Cr. Def. (mm) $\sigma$=0.7·TYS $\beta$=1.1 |
|---|---|---|
| API 5AC C90 | - | - |
| AISI 4137H | 9 | 0.05 |
| | 6 | 0.02 |
| AISI 420 (API 5AC C90) | 26 | 0.85 |
| | 37 | 1.73 |
| 22Cr-5.5Ni-3Mo | 43 | 1.03 |
| | 50 | 1.40 |
| 27Cr-31Ni-3.5Mo | 61 | 3.37 |
| | - | - |

Tab. 4 - Critical defects of the tested steels ($\sigma$=0.7·TYS - $\beta$=1.1)

## 5 - FRACTOGRAPHIC ANALYSIS

In Fig. 7 some macro and micro fractographies of smooth specimens are shown. The documentation shown there for each material is referred to one environment and one stress level only. It was not revealed as an important difference between specimens of the same material loaded to different stress levels, or any of the two environments.

The fracture surfaces show more or less width areas of intergranular fracture (i.e. along the boundaries of the old austenitic grains) in AISI 4137 H and AISI 420 (API 5AC C90) steels. API 5AC L80 steel instead, falls in transgranular cracking. The specimens have also revealed more or less numerous perpendicular cracks to the stress direction and cracks parallel to the crack that lead to specimen failure.

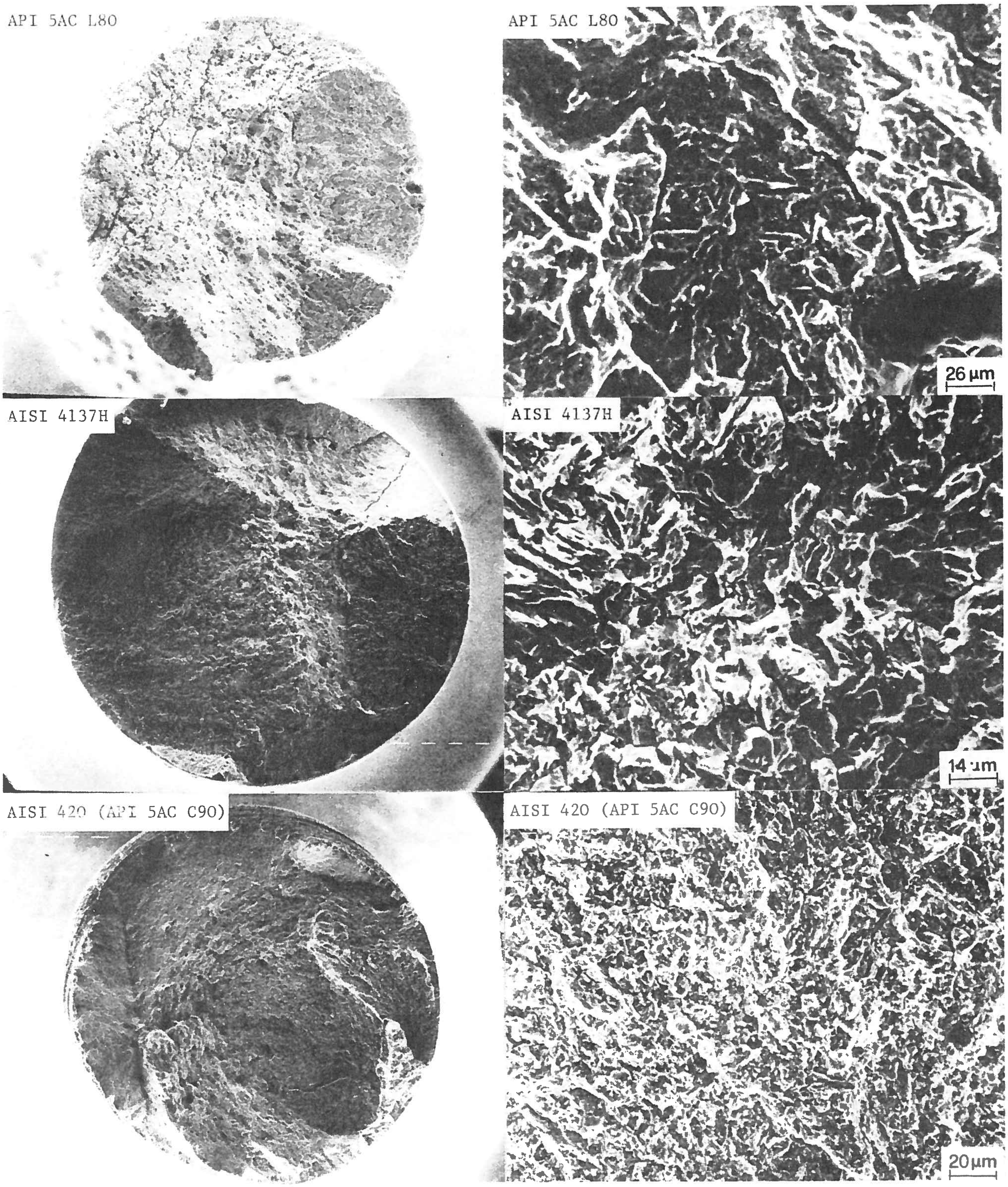



Fig. 7 - Macro and micro fractographies of smooth specimens.

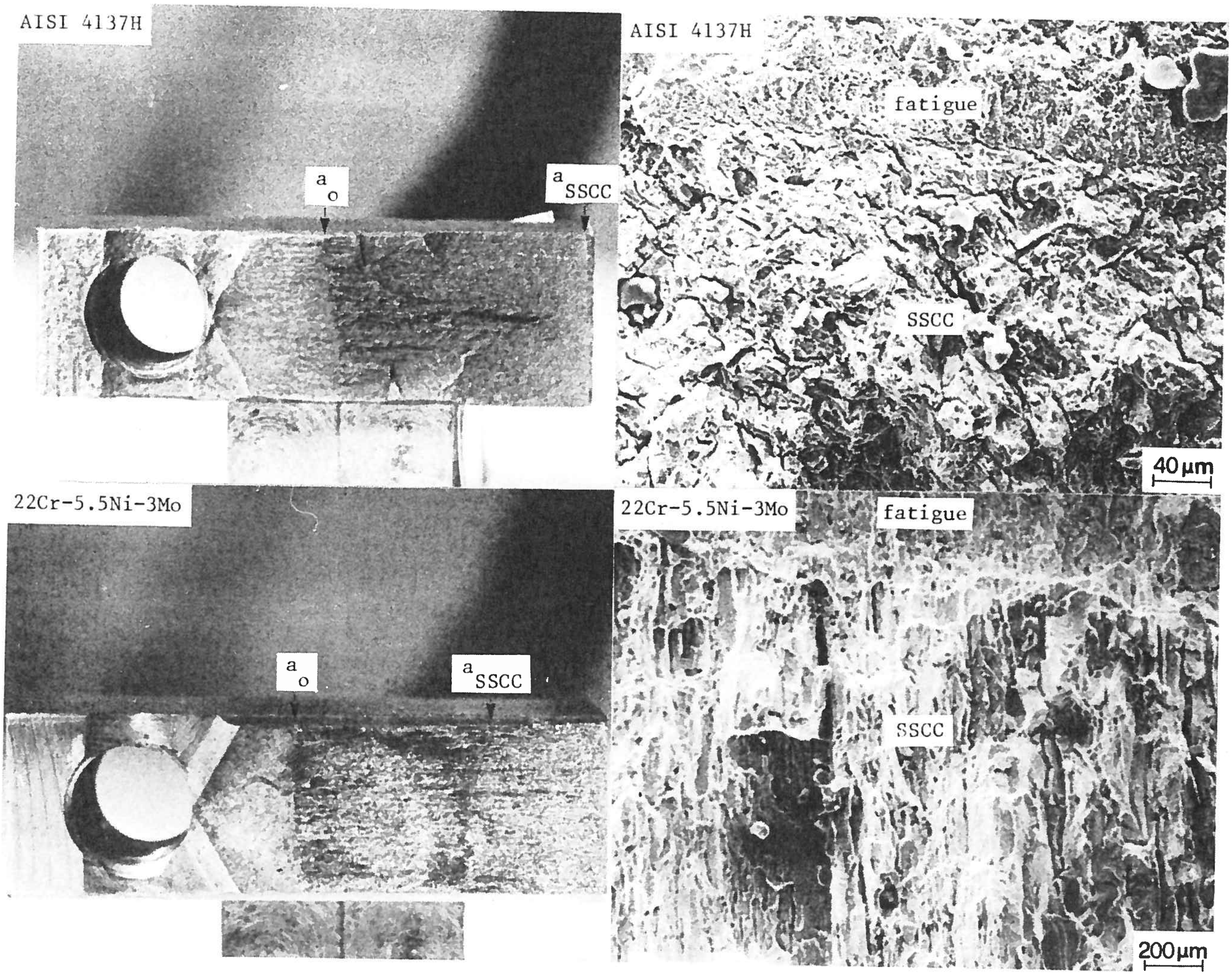



Fig. 8 - Macro and micro fractographies of 1/2" thick WOL-modified specimens.

As far as precracked specimens are concerned, Fig. 8 shows a macro and micro fractographies for one specimen of each material.

The fractographic observations coincide solely with those taken on smooth specimens for AISI 4137H. Regarding the 22Cr-5.5Ni-3Mo duplex stainless steel, it can be noted that the SSCC crack is of a transgranular type.

## 6 - CONCLUSIONS

From the analysis of the results some conclusions can be drawn.

As have been demonstrated from the preceding work on this and other steels (19-20), the impossibility of using carbon or low alloy steels at high strength levels can be confirmed when relevant $H_2S$ contents are present.

The good behaviour of duplex and superaustenitic cold worked steels can also be confirmed when using smooth specimens.

The proofs of fracture mechanics specimens instead, show how the results on smooth specimens cannot be extrapolated in conditions in which sharp defects may be present (see the results on duplex stainless steel). In particular the usability diagrams of steels should be correlated with the maximum dimension of the defects that are present (due to the fabrication or put into operation of the same) or with the dimensions that would have been revealed with non-destroying analysis.

The use of a constant deformation WOL-modified specimen is notably interesting for testing in real environments due to the compactness that characterises this specimen.

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We would like to give our tribute to Professor Dany Sinigaglia, a dear friend and distinguished scientist, who helped initiate this research, but who sadly passed away on 10/7/1983.

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