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The Susceptibility of 12 per cent Chromium Steels to Stress–Corrosion Cracking

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The susceptibility to stress corrosion of three 12 per cent chromium steels of different microstructure was evaluated by the use of slow strain-rate tests in the NACE TM-01-77 environment or after charging with hydrogen in the presence of arsenic. It was found that all the steels were susceptible to sulphide stress–corrosion cracking (SCC) and, to a lesser extent, to SCC in the hydrogen-charged condition. The difference in the susceptibility to SCC of the steels was explained in terms of differences in their hardness, the microstructure having little influence on SCC under these conditions. The steel with an equi-axed structure of ferrite performed marginally better than those with a fine microstructure consisting of martensite and ferrite.

Introduction

The use of alloys with a chromium content of about 12 per cent is attractive from an economic point of view since this is the approximate minimum chromium content at which a steel will passify spontaneously in many environments. Typical applications are in localities where the corrosion resistance of low-alloy steels is inadequate but the use of highly alloyed stainless steels is not warranted from a cost point of view. The corrosion resistance of these steels lies somewhere between that of mild steel and that of the more highly alloyed stainless steels. Like other high-chromium steels, 12 per cent chromium steels are susceptible to localized corrosion phenomena such as crevice corrosion, pitting corrosion, and stress–corrosion cracking (SCC). The emphasis of this paper is on the resistance to SCC of three 12 per cent chromium steels.

Steels containing only chromium as a major alloying element are not susceptible to SCC in hot solutions containing chloride[1], but are somewhat sensitive to hydrogen-induced SCC depending on the metallurgical condition. This is of particular importance in the petroleum industry, where process conditions are favourable for the entry of hydrogen into steel. Examples of this range from high-temperature and high-pressure exposures in hydrogen-containing gases to low-temperature aqueous solutions, where the reduction of hydrogen ions liberates hydrogen on the surface of the metal. The latter phenomenon is the subject of the present paper. The amount of hydrogen that will enter steel depends on a variety of factors, with the presence in the solution of so-called hydrogen poisons, such as arsenic and sulphide species, playing a particularly important role. Sulphur species are often present in crude oil and gas, and induce various hydrogen-related problems in steels, such as hydrogen blistering and sulphide stress–corrosion cracking (SSCC)[2].

The properties of a steel such as its chemical composition, microstructure, and flow stress determine the influence of hydrogen on it. The chemical composition largely determines the quality of the surface films that form and have to be ruptured in some way or another to allow corrosion and the coupled generation and ingress of hydrogen into the steel. The minimum chromium content needed for the formation of a passive film on steel depends on the aggressivity of the environment, which is to a large extent determined by the pH, chloride and sulphide contents, and temperature of the environment. Once localized corrosion has been initiated, the pH and chloride content of the localized environment is increased, which stimulates further attack and hydrogen entry into the steel. The role of sulphides is probably to depassify the steel to some extent by the formation of less protective sulphide-containing corrosion products and also to stimulate the entry of hydrogen into the steel[3,4].

The microstructure of steel is a function of its chemical composition and thermo-mechanical history. The microstructure of 12 per cent chromium steels depends primarily on the amount of austenite present at high temperatures. The austenite–ferrite balance is sensitive to the chemical composition of steel. Austenite stabilizers, in particular the interstitial elements carbon and nitrogen, increase the maximum amount of austenite that is stable at high temperatures. Depending on the cooling rate, the austenite can be transformed to either ferrite or martensite. The hardenability of these steels is generally high, making possible the transformation to martensite during air cooling. The microstructure of 12 per cent chromium steels ranges, from fully martensitic for high-carbon steels cooled in air from the austenite regime, to a ferrite–martensite structure for steels with intermediate carbon, and to a fully ferritic structure for steels annealed in the ferrite-phase domain.

The present work concerns the evaluation of the SSCC resistance of a number of 12 per cent chromium steels of low carbon content with microstructures ranging from equiaxed ferrite (steel A) to elongated ferrite interspaced with tempered martensite (steels B and C). In the latter two steels, the grain size was also significantly smaller. It can be expected that the elongated grains may offer some additional resistance to cracking in the transverse direction if the cracking is intergranular in nature due to crack blunting. Another notable difference between the steels is that, in steel A, most of the carbon is probably present in the form of massive carbides that are widely interspaced while, in the other two steels (B and C), the carbides are much smaller.

The form of the interaction between hydrogen and steel depends on the flow stress of the steel. As a general guide, steels with a flow stress of less than 700 MPa are not very sensitive to hydrogen-induced embrittlement but are more likely to form hydrogen blisters[5]. This fact is covered in the NACE specification for the SSCC of steels that are to be used in sulphide-containing environments[6], where a maximum hardness of 22 Rockwell C is specified for 12 per cent chromium steels to limit the possible occurrence of SSCC. There is no obvious theoretical basis for the choice of this hardness apart from the fact that the critical defect size for this hardness is approximately that which has been observed in inspections[7]. It is therefore not surprising that SSCC sometimes occurs below that strength level[8].

Experimental Procedure

The chemical compositions of the steels studied are given in Table I. The resistance of several steels containing approximately 12 per cent chromium to SSCC and hydrogen embrittlement were evaluated by slow strain-rate tests (SSRT) in the environment specified in NACE standard[9] TM-01-77, or after cathodic charging with hydrogen in the presence of arsenic. The charging with hydrogen was used to simulate conditions that could develop during long-term exposures and also to avoid incubation effects that would seriously affect the results of the SSRT owing to the short exposure times in these tests. Although SSRT are not specified in the NACE specification, they make use of a well-established technique [10-12] for the evaluation of SSCC.

TABLE I
CHEMICAL COMPOSITION OF THE STEELS EVALUATED, WT%

Steel	C	Si	Mn	Ni	Cr	Ti	N
A	0,020	0,25	0,32	0,15	12,25	0,004	0,0266
B	0,023	0,40	0,98	0,19	11,55	0,005	0,0138
C	0,021	0,47	1,18	0,22	11,24	0,010	0,0104

The SSRT were conducted by straining the specimen in a Hounsfield tensiometer fitted with a slow drive and using an initial strain rate of 2,6 x $10^{-5}s^{-1}$. An aqueous solution containing 5 per cent NaCl and 0,5 per cent acetic acid that was saturated with H_2S was used as the corrosive environment in the SSCC experiments. The solution was circulated continuously from a reservoir of 2 dm^3 to the cell. The solution was de-aerated with nitrogen for 2 hours before it was saturated with H_2S. The temperature of the solution was kept constant at 24 °C throughout the test. The applied stress and the elongation of the specimen were recorded continuously during the test. A schematic view of the test cell is shown in Figure 1.

In the cathodic-charging experiments, the samples were charged with hydrogen in a 10 per cent sulphuric acid solution containing 0,5 g/l of As_2O_3 at a current density of 50 mA/cm^2 for 24 hours. The SSRT were run shortly after the charging, the charging and the tests being conducted at room temperature.

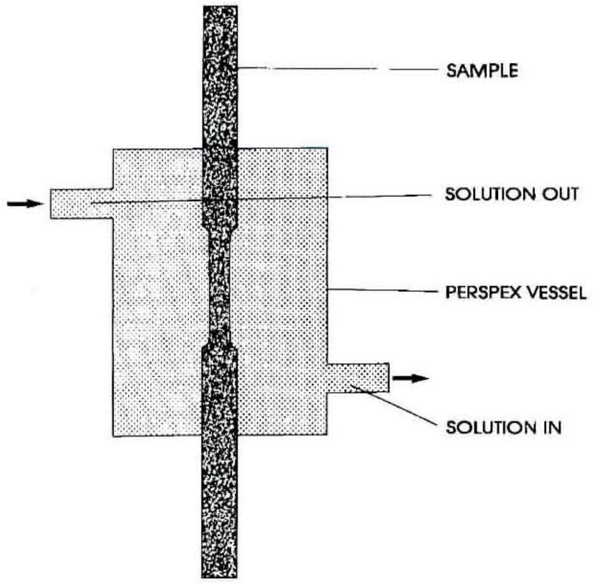

FIGURE 1. Schematic view of the test cell used in the slow strain-rate tests

Results and Discussion

Typical stress–strain relationships during the testing of a 12 per cent chromium specimen are shown in Figure 2, and the results of the various SSRT runs are summarized in Table II. It is clear that both steels were susceptible to SSCC, as indicated by the significant reduction in strain at failure obtained in the NACE solution. The elongation achieved in an H_2S environment was around 0,03 of the elongation in air for steel A. For steel B, the corresponding figure was 0,26. The value for steel C was 0,24. The difference in the susceptibility of these two steels to SSCC could

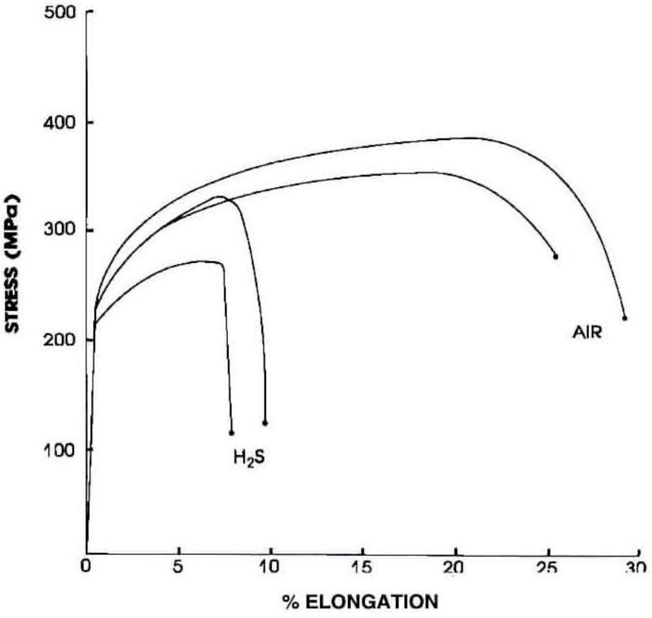

FIGURE 2. Typical stress–strain relationships during the testing of 12 per cent chromium specimen in various environments. Initial strain rate 2,6 x $10^{-5}s^{-1}$ (steel A)

TABLE II
RESULTS OBTAINED IN SLOW STRAIN-RATE TESTS ON 12 PER CENT CHROMIUM STEELS

Environment	Steel	Tensile strength, R_m MPa	Elongation, A %	Hardness, R_B
Air	A	390	29	77
		360	25	
	B	460	24	82
		475	23	
	C	500	18	80
		505	15	
5% NaCl + 0,5% acetic acid + H_2S at 24 °C	A	210	7,2	77
		277	8,0	
		336	9,4	
	B	323	6,6	82
		325	5,6	
	C	412	4,0	80
Hydrogen charging (50 mA/cm² for 24 h in 10% H_2SO_4 + 0,5g/l A_32O_3	A	326	24	77
	C	509	3,6	80

probably be explained largely by the difference in hardness. The hardness of steel A was 77R$_B$, steel B was 82R$_B$, and steel C was 80R$_B$. The relatively poor performance of steel C, given that its hardness was lower than that of steel B, was probably due to the fact that these samples were stressed transverse to the rolling direction.

It can be argued that the NACE test solution is too severe an environment for this type of steel, and that milder conditions should be used if the difference in the resistance of the steels to hydrogen is to be established. The results obtained for some of the steels in the SSRT after hydrogen charging for 24 hours are also shown in Table II. The tensile elongation in hydrogen charging was around 0,90 of that of the specimen tested in air for steel A. For steel C, the corresponding figure was 0,21. The difference between the equiaxed material (steel A) and the steels with elongated structures was much more pronounced in this less aggressive environment. The higher elongation achieved in hydrogen-charging conditions by steel A reflects the lower severity of the second SCC environment.

The primary stress–corrosion cracks (those cracks perpendicular to the direction of tensile stress) were generally transgranular, as can be seen from Figure 3, which shows the appearance of such a crack on a polished section transverse to the original thickness of the rolled plate. In Figure 3 the photomicrograph was so oriented that the magnification bar was parallel to the direction of the tensile stress during slow strain-rate testing. The secondary stress–corrosion cracks were generally intergranular. Again, scanning electron microscope (SEM) images of the fracture surfaces (Figures 4 to 6) show the mainly transgranular nature of the fracture surface of these steels, but also the intergranular cracking perpendicular to the main crack. The relatively flat surface of the crack indicates that the SSCC behaviour of these steels was largely insensitive to the scale of the microstructure. Lamellar tearing exhibited by steel C is illustrated by the fracture surface shown in Figure 6.

FIGURE 3. Microstructure of material surrounding a sulphide stress–corrosion crack in steel B, showing the duplex structure of the highly elongated, fine ferrite–martensite grains

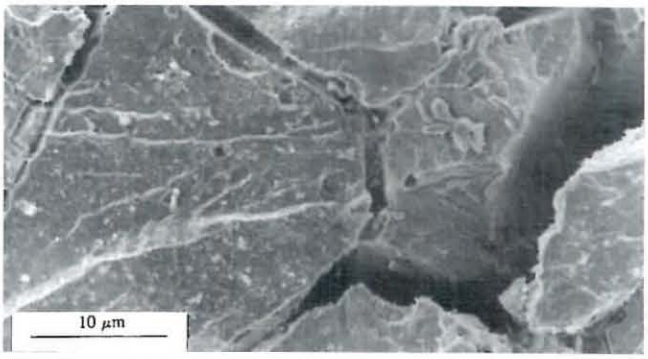

FIGURE 4. Fracture surface of a sulphide stress–corrosion crack in steel A, showing largely transgranular fracture (secondary electron image, accelerating voltage 8 kV)

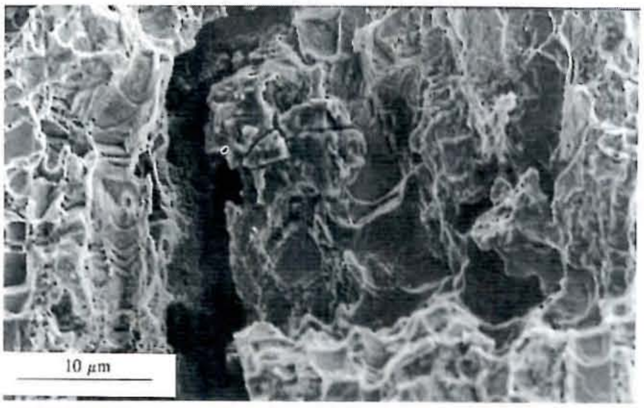

FIGURE 5. Fracture surface of a sulphide stress–corrosion crack in steel B, showing its transgranular nature (secondary electron image, accelerating voltage 8 kV)

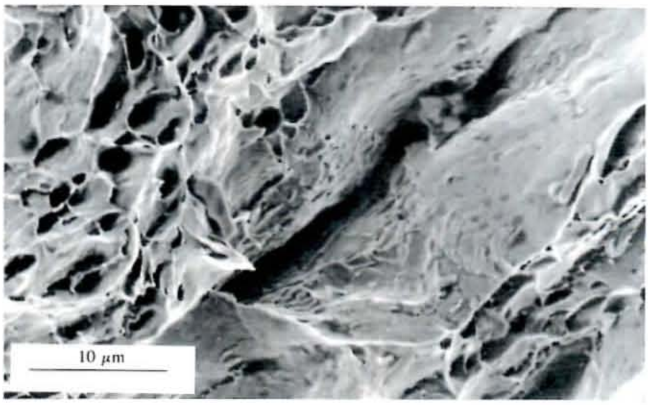

FIGURE 6. Fracture surface of a stress–corrosion crack in steel C after hydrogen charging for 24 hours. Two regions where ductile fracture occurred are separated by an area of lamellar tearing (secondary electron image, accelerating voltage 8 kV)

It was rather surprising that the elongated grain structure did not significantly inhibit crack growth in the transverse direction. This is indicative of the severe susceptibility of the steel to this type of cracking. The presence of martensite in steel B would also increase the susceptibility to SSCC. These results would therefore indicate that the harder steels are the more susceptible, and that a fine-grained duplex structure is not necessarily beneficial in this regard.

Conclusions

(1) The 12 per cent chromium steels evaluated were susceptible to SSCC in the NACE environment and under hydrogen-charging conditions, the latter environment being significantly less severe.
(2) The difference in hardness could largely explain the difference in susceptibility to SCC.
(3) A fine microstructure consisting of martensite and ferrite did not significantly improve the resistance to cracking.

Acknowledgments

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