Research Article

Environmental and Material Influences on the Stress-Corrosion Cracking of Steel in H_2O – CO – CO_2 Solutions

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Received 14 March 2012; Revised 18 April 2012; Accepted 26 April 2012

Academic Editor: Rokuro Nishimura

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The stress-corrosion cracking of A516 pressure vessel steel was investigated by the use of slow strain-rate tests. The orientation of samples to the rolling direction was investigated, and it was found that samples machined longitudinal to the rolling direction showed a slightly increased sensitivity to stress corrosion. The temperature variation showed that for different gas mixtures, the maximum sensitivity to stress corrosion was in the region of 45° to 55°C for the 25% CO gas mixture, whereas with higher CO concentrations, this temperature region of maximum sensitivity moved to higher temperatures. Surface finish showed a slight increase in sensitivity to cracking with increased surface roughness. The most significant increase was found with increased total gas pressures and when samples have been exposed to the environment for an extended period. This was as a result of the inhibition of the corrosion reaction by the passivation of the carbon monoxide, which is a time-dependent process.

1. Introduction

During coal gasification processes, a significant volume of water comes in contact with the combustion gas mixture, and the result of this is a contaminated, black water by-product that is transported and processed. Due to water shortages, the by-product water is used as a cooling agent. This water by-product then comes in contact with steel piping which leads to embrittlement thereof during exposure to the appropriate conditions. The water by-product consists of water with dissolved gasses mainly as carbon monoxide and carbon dioxide. Steel is susceptible to stress-corrosion cracking (SCC) in $\text{CO}/\text{CO}_2/\text{H}_2\text{O}$ environments. Extensive research [1, 2] has indicated that SCC in this system is probably due to inhibition of iron corrosion in the H_2O – CO_2 system by the time-dependent adsorption of CO. Rupture of the inhibited passive surface by emerging slip steps then creates the highly localised active region on a passive surface necessary for the development of a sharp crack. Previous work done by various researchers [1–3] using a wide spectrum of mechanical tests and potentiodynamic polarisation has indicated that SCC of steel in this system occurs over a wide range of

CO partial pressures and temperatures which include the typical operating conditions for coal gasification plants. This indicated that high susceptibility to SCC has not always been found in the plant, from personal experience, where SCC is indeed limited to certain areas of the plant. Malik [4] performed an investigation on steel exposed to the vapour phase of H_2O – CO – CO_2 mixtures and found that in the presence of both carbon monoxide and carbon dioxide, the steel was more sensitive to cracking.

This investigation concentrated on the effect of temperature, carbon monoxide concentration, pressure, sample orientation, and surface finish on the susceptibility to cracking of carbon-manganese steels. The slow strain-rate test technique was used since it is a simple test to discriminate between environments and material conditions to reveal the relative sensitivities to cracking. With the appropriate strain rate, it is possible to induce stress-corrosion cracking. The most important characteristic of the test is the relatively slow strain rate generated at the region of crack initiation and growth. A principle advantage of the test is the rapidity with which the stress-corrosion susceptibility may be assessed. For many systems, a tensile strain rate of 10^{-5} to 10^{-6} s^{-1}

TABLE 1: The A516 pressure vessel steel composition.

Element	Al	B	C	Co	Cr	Cu	V	Mn
wt%	0.009	0.002	0.217	0.010	0.010	0.010	0.010	1.030
Element	Mo	N ₂	Nb	Ni	P	S	Ti	Si
wt%	0.010	0.007	0.004	0.020	0.009	0.003	0.001	0.290

FIGURE 1: A schematic presentation of the tensile specimen in the autoclave that was used for the slow strain-rate test.

promotes cracking, but the absence of embrittlement at these rates would not be indicative of immunity to cracking if other strain rates have not been investigated. Generally, the strain rate is constant for most of the test, but as soon as the necking starts, the localised strain rate increases dramatically, and the sensitivity to cracking diminishes. However, at this stage, the cracks have formed already, and the ductile failure induced by the higher strain rates is reduced, because of the existing cracks that formed during the uniform strain-rate application. The effective strain rate once cracks have initiated cannot be measured. With the slow strain-rate test it is possible to control the rate-determining step which is the strain rate of the deforming specimen.

Comparison between identical specimens exposed to the embrittling environment and inert conditions can be used to assess the susceptibility to cracking. In this study, the parameters used were the percentage elongation, as well as the percentage reduction in area, as these are easily measured.

The stress-corrosion cracking characteristics of A516 pressure vessel steel were investigated in terms of the influence of the gas composition, rolling direction,

temperature, total gas pressure, applied electrochemical potential, time of exposure before testing, surface finish, and strain rate. The interrelationship of these factors was investigated to determine conditions of maximum susceptibility to cracking.

2. Experimental Procedure

2.1. Material. The steel used throughout the study was A516 pressure vessel steel, with the composition shown in Table 1. The composition was determined by using Leco Carbon/Sulphur Analysers, 3460 Emission Spectrometer, and 8680 + 72RET XRF Spectrometers.

Stress-corrosion cracking was evaluated by using the slow strain-rate method according to ISO 7539-7 (ASTM E8), with the initial slow strain rate being 10^{-6} s^{-1} . A schematic drawing of the test rig used is shown in Figure 1.

The environment consisted of distilled water saturated with a CO/CO_2 gas mixture. Small-sized specimens proportional to the standard specimen according to ASTM

standard E8 for cylindrical tensile test specimens were used, with a diameter of 4.0 mm and a reduced section length of 22.5 mm, slightly longer than the standard which is at 19.0 mm a schematic drawing of the tensile specimen is shown in Figure 2.

2.2. Experimental Procedure. The water-gas mixture was prepared in a stainless steel pressure vessel of approximately 160 litres. This setup was also used for the other laboratory tests performed during this study. The pressure vessel was filled with distilled water and purged with nitrogen for long enough to ensure that the dissolved oxygen concentration was below 0.1 ppm. Following the nitrogen purge, there was a purge with the appropriate gas mixture for approximately 20 minutes, and thereafter, the vessel was sealed and pressurised to the required level. Most of the experiments for the slow strain-rate tests were performed at a pressure of 800 kPa and a gas composition of 25% carbon monoxide and 75% carbon dioxide. The gas mixture was prepared beforehand by a commercial gas company according to the required concentrations.

The prepared solution was then transferred to the cell with the slow strain-rate tensile specimen as shown in Figure 1. The solution was allowed to flow through this unit to ensure that the same conditions were achieved in the environment of the tensile specimen. The temperature was measured with a K-type thermocouple that was introduced into the autoclave with a Swagelok fitting, and the temperature was controlled by a temperature controller that regulated a heating element which was wrapped around the autoclave. The pressure in the slow strain-rate autoclave was measured with a pressure gauge that was also introduced into the autoclave with a 1/8" stainless steel tube and Swagelok fitting. Two Viton seals were used to seal and insulate tensile specimen from the autoclave. The autoclave was manufactured from stainless steel which would have shown insignificant corrosion with very little contamination. Each tensile specimen was further insulated from the testing rig at the pulling rod ends, to ensure that no galvanic cell was formed between the stainless steel autoclave and the carbon steel specimen.

With most of the tests, unless otherwise noted, the specimen was installed in the autoclave, after which the autoclave was filled with the solution, and the test was started shortly afterwards. The tensile specimen was also slightly prestressed to ensure that no time was wasted during the tensioning of the frame and pulling rods, since the strain-rate was low and this would have increased the duration of the test considerably.

The specimen was measured beforehand with a vernier calliper in terms of its gauge length and original diameter. The accuracy of these measurements was to the nearest 0.1 mm, according to the accuracy of the vernier calliper. The gauge length measurements were made from shoulder to shoulder on the tensile specimen, which included the radii where no elongation would be expected, but these positions were the best defined and consistent on all the specimens. The original and final diameters were measured, and the final

diameter, after the test, was measured by carefully rejoining the two fractured pieces. This measurement was difficult and the accuracy disputable with a definite higher margin of error.

3. Results

The results from the slow strain-rate tests for samples machined parallel to the rolling direction are shown in Table 2. Here, the lengths of the two fractured sections were given as l_1 and l_2 ; therefore, l_f the final length of the specimen, was

$$l_{\text{final}} = l_1 + l_2. \quad (1)$$

The elongation of the specimen was calculated as follows:

$$\text{Elongation} = \frac{l_{\text{final}} - l_0}{l_0} \times 100, \quad (2)$$

where l_0 was the original length of the specimen, measured from shoulder to shoulder. The reduction in area was given by

$$\text{Reduction in area} = \frac{d_0^2 - d_{\text{final}}^2}{d_0^2} \times 100, \quad (3)$$

where d_0 was the original diameter, and d_{final} was the final diameter of the gauge length of the sample. Table 3 gives the results of the samples tested perpendicular to the rolling direction. These results are further presented in Figure 3 to Figure 7. Figures 3 and 4 show the influence of the orientation of the specimens to the rolling direction of the plate, as well as the environment temperature in terms of the reduction in area and elongation, respectively. The stress-corrosion cracking susceptibility was demonstrated by the loss in the reduction in area, as well as elongation. The errors were calculated by considering the accuracy of the measuring equipment, and especially on the reduction in area the error was more significant. These results did not show considerable repeatability; however, the reason for this was established during the course of the investigation. The influence of rolling direction on the susceptibility to cracking was not significant, and it would appear that stress-corrosion was affected to a greater extent by the environmental parameters, such as temperature, rather than material parameters.

Figure 5 illustrates the influence of the total pressure of the medium on the susceptibility to cracking in terms of the elongation and reduction in area. These results were for samples machined parallel to the rolling direction at a temperature of 45°C.

The effect of the total gas pressure on the cracking sensitivity exposed to a 25% carbon monoxide environment is shown in Figures 5 and 6. From these two figures, it appears that the increase in pressure has a significant effect on the crack sensitivity; with higher overall gas pressures the steel becomes more embrittled than for similar conditions at lower pressures. In Figure 5, it is shown that at 20°C an increase in the total gas pressure causes a drop in the reduction in area measured on the samples. When the

FIGURE 2: The configuration of the tensile specimen used.

FIGURE 3: Elongation as a function of temperature for specimens machined longitudinal and transverse to the rolling direction, at 800 kPa with a gas mixture of 25% CO and 75% CO₂.

FIGURE 4: Reduction in area as a function of temperature for specimens machined longitudinal and transverse to the rolling direction, at 800 kPa with a gas mixture of 25% CO and 75% CO₂.

TABLE 2: Temperature-dependent results of samples machined parallel to the rolling direction.

Sample	Temperature (°C)	Total pressure (kPa)	l_1 (mm)	l_2 (mm)	l_{final} (mm)	Elongation (%)	d_{final} (mm)	Reduction in area (%)
L1	20	350	10.3	23.7	34.0	17.8	3.05	41.8
L3	20	500	23.8	10.35	34.15	18.4	3.20	36.0
L15	20	800	14.1	20.3	34.4	19.6	3.30	31.9
L13	20	1000	23.6	10.1	33.7	16.4	3.55	21.2
L10	20	Air	11.0	25.5	36.5	28.9	2.20	69.8
L16	30	800	11.2	22.8	34.0	17.8	3.35	30.3
L7	35	800	10.2	22.1	32.3	10.2	3.68	15.6
L4	35	800	12.5	21.4	33.9	17.3	3.30	31.9
L9	40	200	23.2	11.7	34.9	21.8	3.00	43.8
L6	40	800	11.1	22.15	33.25	14.4	3.45	25.6
L8	45	800	23.2	10.2	33.4	15.1	3.55	21.2
L14	50	800	20.5	12.5	32.0	13.5	3.45	25.6
L17	60	800	24.7	8.5	33.2	14.4	3.35	29.4

* This total length includes the shoulders of the specimen and does not refer to the gauge length.

TABLE 3: Temperature-dependent results of samples machined perpendicular to the rolling direction.

Sample	Temperature (°C)	Total pressure (kPa)	l_1 (mm)	l_2 (mm)	l_{total} (mm)	Elongation (%)	d_{final} (mm)	Reduction in area (%)
K7	20	800	24.55	10.50	35.05	22.4	3.12	39.2
K4	20	1000	15.10	20.00	35.10	22.7	3.1	39.9
K9	30	800	23.15	10.40	33.55	15.8	3.17	37.2
K2	35	800	17.20	17.50	34.70	20.8	3.15	38.0
K6	35	1000	15.50	18.25	33.75	16.7	3.42	26.9
K1	45	1000	20.55	12.45	33.0	13.3	3.55	21.2
K5	45	800	15.70	17.50	33.20	14.2	3.7	14.4
K8	50	800	24.95	7.80	32.75	12.2	3.65	16.7
K11	60	1000	24.40	9.20	33.6	16.0	3.34	30.3

influence of the total gas pressure was evaluated at various temperatures, as shown in Figure 6, the effect of the total gas pressure was not as significant.

The influence of the temperature on transverse samples exposed to 50% carbon monoxide and 50% carbon dioxide was investigated, and the detailed results are shown in Table 4. The tests were performed at 800 kPa.

The test results shown in Table 4 were similar to the results of the tests performed in 25% CO and 75% CO₂, where there existed a range of greater stress-corrosion susceptibility for the intermediate temperatures, such as from 40°C to 60°C.

Figure 7 shows the reduction in area as well as the elongation for samples that were tested in 50% carbon monoxide and 50% carbon dioxide evaluated over a range of temperatures, between 20°C and 80°C.

The test results are compared later in Figure 8 for the two gas compositions evaluated, namely, 25% and 50% carbon monoxide; the maximum sensitivity increased to higher temperature for the 50% carbon monoxide.

The electrochemical potential dependence was investigated by using a *Voltamograph* CV-27 potentiostat to keep the sample at a certain potential for the whole duration of

the slow strain-rate test. These tests were performed at 45°C, 800 kPa, and a carbon monoxide concentration of 25% and 75% carbon dioxide. The potential was measured with an Ag/AgCl reference electrode that was introduced into the autoclave by a Luggin probe. The results are shown in Table 5, where the embrittling factor is plotted as a function of the applied electrochemical potential in terms of the Ag/AgCl reference electrode.

The results shown above in Table 5 are illustrated in Figures 9 and 10, demonstrating the effect of applied potential on elongation and reduction in area, respectively.

From both figures, it is clear that at a particular applied potential range, the cracking sensitivity of the steel was more enhanced.

The effect of surface roughness was investigated when scanning electron micrographs showed crack initiation on grinding marks as seen in Figures 11 and 12. Here, the cracks formed on what seems to be a 45° angle, which turned out to be the grinding angle for the specific sample. Slow strain-rate tests were performed on samples with different surface finishes. Grinding papers with the following ISO/FEPA grit designation grit sizes: P180, P200, P400, P600, P800, and P1200 were used on separate samples, where the P180 is the

FIGURE 5: Reduction in area and elongation as a function of pressure of slow strain-rate tests performed at 20°C with a gas mixture of 25% CO and 75% CO₂.

FIGURE 6: Comparison of two pressures over a temperature range with regard to reduction in area for a 25% CO and 75% CO₂ gas mixture.

roughest and P1200 is the smoothest paper, and the average particle diameters are approximately 82, 75, 35, 26, 22, and 15 μm . Table 6 shows the results of these tests performed on samples exposed to 25% carbon monoxide and 75% carbon dioxide, at 45°C and 800 kPa. Figures 13 and 14 show the results of the slow strain-rate tests in terms of the reduction in area and elongation; here, it can be seen that elongation did not show a marked difference in the influence of the machining marks on the surface of the samples. However, on the reduction in area results, a decrease was found, a greater susceptibility, with increasing surface roughness. This trend is slightly masked by scatter in the results.

The time of exposure of the specimen to the solution before test was started was investigated when it accidentally became evident that a specimen showed increased brittleness when the test was not performed immediately. In Figure 15, the embrittling factor index is plotted against the time of exposure prior to testing. For these exposure tests, the experimental parameters were a total gas pressure of 800 kPa, a temperature of 45°C, and a strain rate of 10^{-6} s^{-1} . Here, the time of exposure before the test had a significant effect on

the embrittling of the sample, which is unexpected, especially considering the degree of embrittling that was found. The embrittling indices for reduction in area and elongation both dropped in the order of 50% when the samples were not exposed to the environment before the test, and when the samples were exposed for 48 hours before testing. This trend was confirmed by the intermediate sample that was only exposed for 24 hours.

The influence of the strain-rate was investigated and in Figure 16 the embrittling factor index is plotted as a function of the strain rate. These tests were also performed at 45°C, 800 kPa, and 25% CO–75% CO₂. The strain-rate varied from 10^{-5} s^{-1} down to 10^{-8} s^{-1} unfortunately only one test was performed at 10^{-8} s^{-1} . The reduction in area index for embrittling increased from 0.2% to 0.4% when the strain rate decreased from 10^{-7} s^{-1} to 10^{-8} s^{-1} , and the same trend was seen on the elongation of the samples it went from slightly above 0.2 to 0.7 when the strain rate was decreased.

In Figure 17 the fracture surface of a specimen tested at 45°C and 800 kPa indicated the typical transgranular cleavage cracking for these tests. Some pearlite colonies are

FIGURE 7: Elongation and reduction in area as a function of temperature for specimens machined transverse to the rolling direction, at 800 kPa with a gas mixture of 50% CO and 50% CO₂.

FIGURE 8: Comparison of results with two different gas mixtures, 25% CO and the other 50% CO.

FIGURE 9: Elongation as a function of the applied electrochemical potential at 800 kPa and 45°C with a gas mixture of 25% CO and 75% CO.

TABLE 4: Temperature-dependent results of samples machined perpendicular to the rolling direction and tested in 50% CO–50% CO₂.

Temperature (°C)	l_1 (mm)	l_2 (mm)	l_{total} (mm)	Elongation (%)	d_{final} (mm)	Reduction in area(%)
25	8.18	25.24	33.42	15	3.06	41
30	10.90	23.26	34.16	18	3.22	35
35	7.84	26.00	33.84	17	3.38	29
40	14.82	18.52	33.34	15	3.50	23
45	13.80	20.92	34.72	21	3.40	28
48	12.42	21.90	34.32	19	3.60	19
50	20.92	12.18	33.10	14	3.56	21
60	12.16	21.00	33.16	14	3.64	17
70	8.94	25.00	33.94	18	3.30	32
75	19.50	14.20	33.70	16	3.48	24

TABLE 5: Potential-dependent results of samples tested in 25% CO–75% CO₂ at 45°C.

Potential (mV)	l_1 (mm)	l_2 (mm)	l_{final} (mm)	Elongation (%)	d_{final} (mm)	Reduction in area (%)
–600	8.9	26.3	35.2	23.11	3.05	41.85
–585	13.2	20.9	34.1	18.1	3.34	30.27
–575	17.8	15.3	33.1	13.6	3.64	17.19
–550	15.8	17.9	33.7	16.4	3.56	21.68
–550	8.0	26.9	34.9	21.86	3.19	36.4
–525	12.9	19.45	32.35	10.4	3.45	25.6
–500	24.9	8.0	32.9	12.98	3.57	20.34
–500	26.15	8.2	34.35	19.5	3.05	41.86
–475	10.95	22.7	33.65	16.2	3.16	37.59
–450	23.8	10.8	34.6	20.8	2.9	47.43

TABLE 6: Results of the slow strain-rate tests performed at 45°C, total pressure of 800 kPa, and 25% CO for different surface finishes.

Sample	Grit finish	Elongation	Reduction in area
L52	P1200	24.0	41.9
L70	P1200	21.7	31.9
L68	P800	22.1	38.4
L59	P600	26.1	36.0
L57	P400	22.8	34.4
L67	P400	16.0	26.0
L63	P220	22.2	31.9
L66	P180	26.2	31.9

seen as the crack propagated through the colony and was possibly etched by the environment. A cross section was also made to show the transgranular nature.

A test was performed in 100% CO, 800 kPa, at a strain rate of 10^{-7} s^{-1} and 45°C. These specimens did show cracking with the elongation at 21.8%.

4. Summary of Results

Here the results of the material and surface characteristics are compared with the environmental influences on the susceptibility of the steel to stress-corrosion cracking.

4.1. Rolling Direction. The results in Figure 4 did not show a significant difference between the two orientations of testing specimens being aligned parallel or perpendicular to the rolling direction, although it did appear that the samples machined longitudinal to the rolling direction showed a slightly higher susceptibility to stress corrosion. At the lower temperature range the samples longitudinal to the rolling direction showed a definitely higher susceptibility. However, at the higher temperatures, between 50°C to 60°C the difference was negligible and in some instances the opposite to the lower temperatures. From both the elongation and reduction in area data, a similar tendency was found.

4.2. Total Pressure. The results in Figure 6 show that according to the % reduction in area, higher pressures increase the susceptibility to stress-corrosion cracking. However, this is in the range of 200 to 1000 kPa. According to the % elongation a similar trend is followed with a slight increase at 800 kPa. It is also seen (Figures 4 and 5) that with an increase in the temperature, the effect of the total pressure is even greater, although this was based on two samples, and more information is needed for statistical certainty. These results are similar to those of Hannah et al. [3] where the reduction in area of the samples decreased with increasing pressures.

FIGURE 10: Reduction in area as a function of the applied electrochemical potential at 800 kPa and 45°C with a gas mixture of 25% CO and 75% CO₂.

FIGURE 11: The influence of grinding marks on crack initiation for a slow strain-rate sample tested at 45°C and 800 kPa 25% CO–75% CO₂.

4.3. Gas Composition. It is clear that at higher carbon monoxide concentrations, the susceptibility to cracking increases dramatically.

4.4. Temperature. The influence of temperature was examined for two situations, samples parallel and perpendicular to the rolling direction.

4.4.1. Samples Perpendicular to the Rolling Direction. When looking at the reduction in area, these samples show a minimum resistance to stress corrosion in the order of 45°C to 55°C. This means that there is an increase in both sides—the region close to room temperature as well as higher temperatures. The increase in the resistance to stress-corrosion cracking at higher temperatures (60°C) was expected with the lower solubility of gases at the higher temperatures.

4.4.2. Samples Parallel to the Rolling Direction. The results show that a similar tendency in sensitivity to temperature for both the samples machined perpendicularly and parallel to the rolling direction. The reduction in area decreased in the temperature range 40°C to 50°C, and this seems to be in agreement with the work of Kowaka [1] as well as

Itoh [5], on the general trend of the effect of temperature. The elongations for these samples gave the same region of greater embrittlement. This behaviour is expected due to the influence of the temperature upon the kinetics of the corrosion reaction and the passivity of the steel. Here, decreased sensitivity to cracking is an indirect effect, due to the decreasing solubility of the carbon monoxide in water at increasing temperatures, which would affect the passivation of the steel. Schmitt and Rothmann [6] also showed a decrease in ductility of various carbon steel with the increase in temperature, from 25°C to 50°C. Although Schmitt et al. [7] found a maximum susceptibility around 40°C for 37 Mn5 steel grades loaded to 90% of yield strength at 10-bar CO₂.

4.5. Applied Electrochemical Potential. In Figure 9, the region where the testing was performed, the cracking resistance increased towards the higher and lower limits. Embrittlement was prevalent from around –575 mV to –475 mV, which is very similar to results obtained by Brown et al. [2]. The fractured specimens at the more noble potentials were characterised by general corrosion and little cracking. Towards the more active limit, hydrogen formation could have induced cracking, but here the resistance to cracking also increased, thus indicating that cracking is not enhanced

FIGURE 12: The same sample as shown above at a slightly higher magnification revealing how the cracks followed the grinding marks on the sample after a slow strain-rate test at 45°C and 800 kPa 25% CO–75% CO₂.

FIGURE 13: Slow strain-rate test results showing the influence of the surface roughness on the stress-corrosion resistance of steel at 45°C and 800 kPa.

by an excess of hydrogen. It could be argued that cracking could still be promoted by the presence of a small amount of hydrogen, but if this was the case, higher concentrations would have decreased the resistance to cracking. The situation is convoluted by the shifting of the corrosion potential with time, but this is evaluated in the next section.

4.6. Time of Exposure. The results in Figure 15 indicated the importance of the adsorbed CO species on the surface of the specimen and the effectiveness of this layer before the sample is stressed. Although only three samples were tested, the trend shows very clearly a greater sensitivity towards cracking. The time of exposure shows a very clear effect on the susceptibility and is a parameter that would cause significant errors if it is not kept constant during testing.

4.7. Surface Finish. The effect of the surface finish was first noted when one of the specimens was studied with the scanning electron microscope, and it was found that cracking occurred along most of the scratches left from the machining and grinding process (Figures 11 and 12). The grinding marks served as crack initiation points. This indicated the sensitivity of the cracking process to crack initiation. Although the influence of grinding grooves was not severe, there was a tendency towards a greater resistance to cracking when the surfaces had finer grinding grooves.

Therefore, it would seem that the crack initiation was more probable with the larger grooves and might be one of the reasons why cracking would occur in one area and not another. The grooving is expected to be similar on the surface, although it is possible that larger grooves remained from previously applied, coarser grinding papers.

4.8. Strain Rate. Strain rate is a very important variable and this was evaluated to a greater extent with other test methods. However, as shown by Kim and Wilde [8], with slow strain-rate testing, it is possible to differentiate between the hydrogen-induced cracking and stress-corrosion cracking. This is because of the repassivation reaction of the steel that prevents the corrosion reaction of the bare steel, since the repassivation occurs at a faster rate than the exposure of the steel due to the slip step emergence. From the results, it is clear that the minimum resistance to cracking is in the order of 10^{-7} s^{-1} . The resistance to cracking increased at 10^{-8} s^{-1} , which means that the passivation rate at the crack tip could keep up with the bare surface that is formed due to the crack tip strain rate. This is an important result that indicates that the cracking is dependent upon the passivation of the steel, and again not the hydrogen embrittlement. Therefore, if the passivation of the steel can be influenced, either by enhancing or breaking it down, the stress-corrosion cracking can be mitigated. Unfortunately, the test at 10^{-8} s^{-1} strain rate was

FIGURE 14: Slow strain-rate test results showing the influence of the surface roughness on the stress-corrosion resistance of steel at 45°C and 800 kPa.

FIGURE 15: The embrittlement of the steel as a function of the time of exposure prior to testing at 45°C and 800 kPa.

performed over a very long period, and only one of these tests was performed; therefore, this is not completely conclusive evidence but suggests that strain rate is a very important component in the cracking process.

5. Discussion

Stress-corrosion cracking of steel exposed to CO–CO₂–H₂O appears to be very dependent upon the carbon monoxide adsorption on the steel surface. With the increase of temperature, the solubility of both carbon monoxide and carbon dioxide decreases and therefore, decreasing sensitivity to cracking was found at higher temperatures. A similar decrease in sensitivity to cracking was found at the lower

temperatures. However, the effect of temperature was moved to higher temperatures for the higher carbon monoxide concentration, therefore indicating the importance of the higher carbon monoxide concentration. The influence of the gas is further highlighted by the effect of higher total gas pressures. Furthermore, the effect of exposure time before the test illustrates the dependence upon the adsorption of the carbon monoxide on the steel interface. This time-dependent adsorption was demonstrated by Heaver [9], illustrating the effect of the passivation of the steel as a result of exposure time to a carbon-monoxide-containing environment. Therefore, when the time dependency of the embrittlement is considered, it has to be ascribed to the adsorption reaction of the carbon monoxide. The other

FIGURE 16: The embrittling factor index as a function of the strain rate of the slow strain-rate test at 45°C and 800 kPa.

FIGURE 17: A scanning electron micrograph of the fractured surface of a slow strain-rate specimen tested in 25% CO at 45°C and 800 kPa total pressure.

parameters that were investigated did not show similar significant embrittling effects. The orientation of the samples and grinding marks on the surface of the samples both did not have a very significant effect, although these parameters showed some contribution to cracking. However, applied potential showed a significant effect on cracking with a definite potential range where cracking was enhanced. The minimum potential to this crack sensitive range corresponded to the corrosion potential and shows insensitivity towards hydrogen charging, whereas the maximum probably corresponded to the transpassive potential. This confirms the importance of the passivation and the passivation kinetics on the crack propagation.

6. Conclusions

- (1) An increase in the total pressure of the gas increases the susceptibility of the steel to stress-corrosion cracking.
- (2) Samples machined longitudinal to the rolling direction showed a slightly increased sensitivity to stress corrosion as compared to those machined transverse to the rolling direction.
- (3) Maximum susceptibility to stress-corrosion cracking is between 40°C and 50°C.
- (4) Cracking is dependent on the electrochemical potential, and cracking decreases on the cathodic side of the polarisation diagram.
- (5) A waiting time before the test is started reduces the resistance to cracking.
- (6) The surface finish does not have a large effect on the cracking resistance, although with a finer finish, the cracking is less.
- (7) Strain-rate dependence shows a maximum susceptibility at around 10^{-7} s^{-1} .

Acknowledgments

The author would like to acknowledge the guidance of Professor R. F. Sandenbergh and Professor G. T. Van Rooyen during the project.

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