IMPACT OF COUPLING TO CARBON STEEL ON HYDROGEN UPTAKE AND CRACKING OF DUPLEX STAINLESS STEEL IN OILFIELD ENVIRONMENTS

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The effect on 22 Cr duplex stainless steel of coupling to carbon-steel in acid brine environments at 80 °C has been evaluated. At low charging currents, hydrogen uptake was independent of pH and H_2S and proportional to the square root of the charging current density, $i^{½}$. At higher charging currents, a critical value was reached above which hydrogen uptake was independent of the charging current density in H_2S-free solution. In H_2S environments, hydrogen uptake remained proportional to $i^{½}$ and independent of the concentration of H_2S. No significant reduction in the strain-to-failure relative to oil was observed in H_2S-free environments. Pre-exposure for 50 days had only a modest effect on the strain-to-failure. In H_2S environments, cracking may occur at coupling currents greater than 100 $\mu A\ cm^{-2}$.

INTRODUCTION

Duplex stainless steels (DSS) are being used increasingly in the oil industry for downhole applications but there is concern about the effect of coupling to carbon steel. This may occur when DSS tubulars are used in conjunction with a carbon steel casing. Ideally, the annulus between the tubular and the casing should be filled with inhibited seawater or man-made brine. However, in practice the joints on the DSS tubular may leak allowing the production fluid to enter the annulus. The production fluid consists primarily of sour acid brine. Hydrogen produced by the coupling reaction will be absorbed into the DSS and may cause embrittlement. Indeed, there has been a notable failure of a cold worked DSS tubular coupled to carbon steel (1).

The aim of the work is to provide guidance on the environmental conditions for which DSS can be coupled to carbon steels without the risk of hydrogen

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embrittlement. To achieve this, galvanic coupling, hydrogen permeation and slow strain rate tests have been undertaken. The coupling tests are designed to establish the coupled currents and potentials. The permeation measurements provide a method for assessing the relative aggressivity of combinations of pH, H_2S and coupling current. A distinctive feature of the cracking tests was pre-exposure of two specimens to the test environment. Hydrogen transport in DSS is very slow and consequently conventional cracking tests are conducted under non-steady-state conditions with respect to hydrogen charging (2). There is concern that the results of short term tests may underestimate the severity of the environmental conditions.

EXPERIMENTAL

Only the essential details of the test techniques and materials are given here as the full details have been described elsewhere (3). To maintain continuity with previous studies (2), the coupling and permeation tests were conducted using SAF 2205, with the composition in wt.% 21.9-Cr, 5.5-Ni, 3.0-Mo, 1.5-Mn, 0.04-C, 0.2-Si, 0.3-N, 0.01-P, 0.001-S, bal. Fe. The volume fraction of austenite was estimated to be 48.9 ± 0.5%. The current trend in DSS is to increase the austenite volume fraction to 55-60%. Therefore, the slow strain rate tests were conducted using 22 Cr DSS with a nominal volume fraction of austenite of 57.2 ± 2.9%. The composition of the steel in wt.% was 21.7-Cr, 5.5-Ni, 3.2-Mo, 1.1-Mn, 0.02-C, 0.3-Si, 0.2-N, 0.02-P, 0.003-S, bal. Fe. The steel had been solution annealed and the nominal 0.2% proof stress was 552 MPa. One permeation test was conducted also with this material.

The test environment was 16.5 g/l NaCl with 4.1 g/l CH_3COONa, based on an early draft of an EFC guidelines document (4). In retrospect, this solution was not ideal in view of the low chloride concentration but the impact for hydrogen uptake under galvanic coupling conditions is considered to be minor. The pH was adjusted to 3.5 or 4.5 using HCl. In all tests, 20 l of solution were pre-conditioned in an aspirator and then recirculated to the test cell. The H_2S content of the solution was measured using the API electrometric titration method. Tests were conducted in H_2S-free solution, H_2S-saturated solution (650 ± 100 ppm (wt.)) and in solution with an H_2S-concentration below 1 ppm (wt.). All tests were carried out at 80 °C.

Galvanic coupling tests

The areas of the carbon steel and duplex stainless steel samples were 70 cm^2 and 3.6 cm^2 respectively, giving an area ratio of 20:1. The specimens were abraded with 600 SiC grit and degreased in ethanol and acetone. Tests were conducted at pH 3.5, with and without H_2S, and at pH 4.5, without H_2S, for periods up to 30 days.

Contamination of the solution with corrosion product was particularly severe during the coupling tests. To avoid this in other types of test and to ensure

experimental control, constant potential or constant current methods were adopted to simulate coupling directly to carbon steel.

Hydrogen permeation testing

The permeation testing was conducted using a two compartment cell in accordance with the draft British standard (6). Membranes were manufactured from the parent material with the orientation such that the permeation flux was perpendicular to the rolling plane of the plate. The membranes were lapped, abraded with 600 grit SiC paper and ultrasonically cleaned.

The solution in the oxidation cell was 0.1M NaOH and the applied potential was +0.300 V (SCE). The solution from the 20 l reservoir was circulated to the charging cell at a linear flow rate past the specimen of about 0.1 cm s^{-1} and flow was further stimulated with a magnetic stirrer. Cathodic charging was applied potentiostatically.

Slow strain rate testing

The slow strain rate tests were conducted according to ISO 7539 Part 7. The specimens used were cylindrical tensile specimens with an overall length of 177.8 mm, a gauge length of 12.7 mm and a diameter of 2.54 mm. The orientation of the specimens was such that the longitudinal axis of the specimen was parallel to the extrusion direction of the bar. They were dry ground to a 1 µm finish and then degreased in ethanol and acetone.

The solution was recirculated from a 20 l aspirator to the cell at a linear flow rate past the specimen of about 0.1 cm s^{-1}. A displacement rate of 1.27×10^{-5} mm s^{-1} was used, giving a nominal strain rate of 1.0×10^{-6} s^{-1}.

In addition to conventional tests, two specimens were pre-exposed to the test environment at 80 °C at a charging current of 0.8 mA cm^{-2} for periods of 28 days and 50 days. Tests were conducted also in oil at 80 °C.

RESULTS

Measurements of duplex stainless steel - carbon steel couples

The potential of the duplex stainless steel - carbon steel couple in H_2S-free solution of pH 3.5 drifted from -620 mV (SCE) to -690 mV (SCE) during the 30 day test. The potentials in H_2S-saturated solution were similar. The steady current density obtained was 105 µA cm^{-2} for H_2S-free solution and 550 µA cm^{-2} for H_2S-saturated solution. The potential of the couple in H_2S-free solution of pH 4.5 drifted from -710 mV (SCE) to -750 mV (SCE) during the more limited 6 day test.

Hydrogen uptake measurements

Hydrogen uptake is plotted vs charging current density, i, in Fig. 1. Hydrogen uptake was defined in terms of C_0, the sub-surface concentration of hydrogen atoms in the lattice per unit volume of material on the charging side of the membrane, and C_t, the total hydrogen content on the charging side of the membrane (3). At low charging currents, hydrogen uptake was independent of pH and H_2S and proportional to $i^{½}$. As the charging current density increased, a critical value was reached above which hydrogen uptake was independent of the charging current in H_2S-free solution. This behaviour is readily explained in terms of a limiting surface coverage associated with increasing efficiency of hydrogen recombination. In H_2S-saturated solution, hydrogen uptake remained proportional to $i^{½}$. In this region, H_2S increased hydrogen uptake by up to a factor of 4. The continued $i^{½}$ dependence in H_2S environments reflects the ability of H_2S to impede the recombination reaction.

The permeation data obtained for the 22 Cr material used in the slow strain rate test are shown also in Fig. 1. The surprising feature is that the permeation data for this very low H_2S solution parallels that for the saturated solution. It is difficult to attribute this simply to differences in the austenite content of the materials since the agreement extends over a range of currents and to the regime of H_2S-free solution. It is more likely that for cathodic polarisation only a monolayer or so of H_2S is required to retard the recombination reactions. This has important implications for the definition of sour service.

Slow strain rate testing

The normalised plastic strain-to-failure in the environment relative to oil is plotted vs hydrogen uptake in Fig. 2, using data from the hydrogen permeation tests. A threshold total hydrogen content for cracking of about 100 ppm(wt.) can be deduced. Hydrogen contents below the threshold are typical of H_2S-free solution. Hydrogen contents above the threshold may be realised in H_2S environments at coupling currents greater than 100 μAcm^{-2}.

Direct comparison with the permeation data for very low H_2S concentrations is difficult since the specific concentrations in the tests were too small to measure. Consequently, there is uncertainty about the value of C_t and this is represented by a band in Fig. 2. The implication of Fig. 2 might be that the concentration of H_2S in solution is below that for the permeation test and below the threshold for significant cracking. Alternatively, the concentrations of H_2S in solution may be similar for the two types of tests but in the slow strain rate test the H_2S concentration at the crack tip may be a more critical factor and this may be reduced to below the critical level. Despite the uncertainty about the value of C_t, it can be concluded that pre-exposure has only a modest effect on the strain-to-failure.

CONCLUSIONS

At low charging currents, hydrogen uptake was independent of pH and H_2S and proportional to the square root of the charging current density, $i^{½}$. At higher charging currents, hydrogen uptake was independent of the charging current in H_2S-free solution but remained proportional to $i^{½}$ in H_2S environments,.

Hydrogen uptake was similar in H_2S-saturated solutions and in solutions with concentrations of H_2S below the measurable level (1 ppm (wt.)). This has implications for the definition of sour service.

The threshold total hydrogen content for cracking under slow strain rate conditions was about 100 ppm (wt.). Hydrogen contents of this magnitude may be generated in H_2S-containing acid brine at coupling currents of 100 $\mu A\ cm^{-2}$.

In H_2S-free environments, the strain-to-failure was similar to that in oil.

Pre-exposure for 50 days had only a modest effect on the strain-to-failure.

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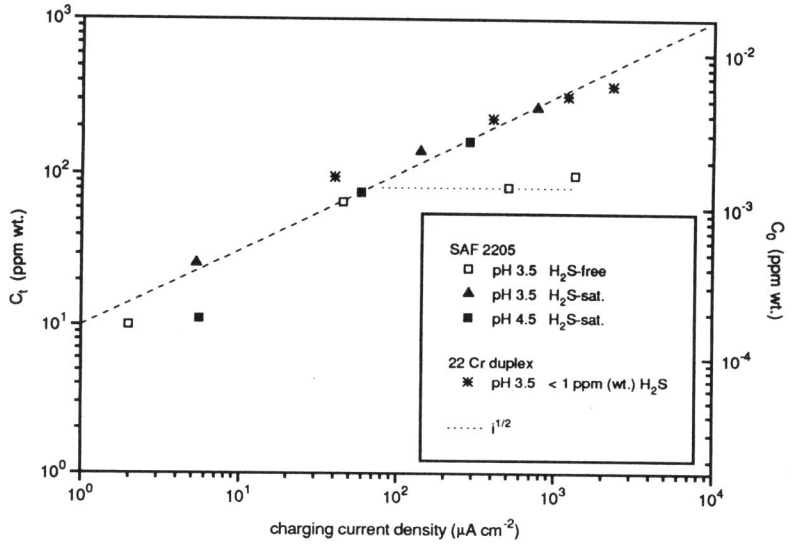

Figure 1 Hydrogen content vs charging current density for 22 Cr duplex stainless steel in acid brine at 80 °C

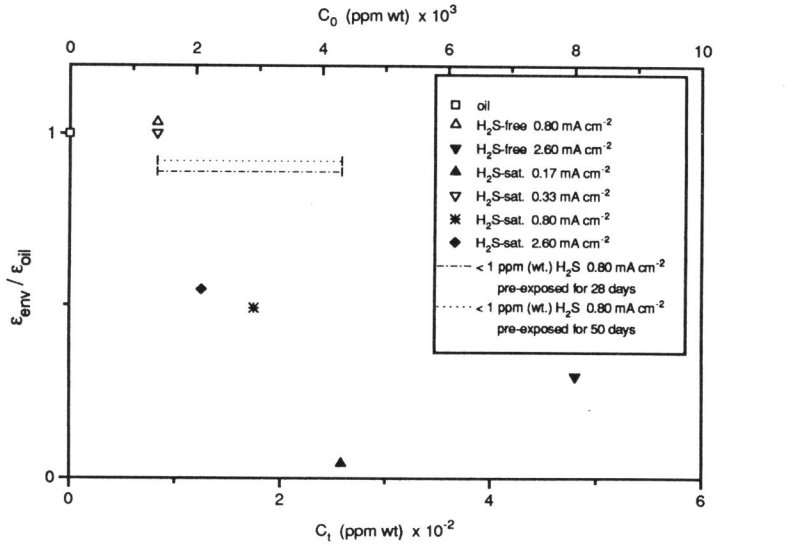

Figure 2 Normalised plastic strain-to-failure vs hydrogen uptake for 22 Cr DSS in acid brine at 80 °C at a nominal strain rate of 1.0 x 10^{-6} s^{-1}