Novel method for determination of pitting susceptibility in aggressive environments at elevated temperature and pressure

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ABSTRACT

Electrochemical characterisation techniques have the potential to reduce the number of expensive and time consuming stress corrosion cracking tests during selection of corrosion resistant alloys for oil and gas applications in which pitting is the precursor to cracking. The main challenge for the application of such techniques is the severity of the environmental conditions. Here we report the development of a novel approach to measurement of pitting susceptibility in very aggressive environments at elevated temperature and pressure based on the use of a high surface area rod specimen with the autoclave seal locally cooled to prevent undesirable crevice corrosion that would compromise the measurement. We also demonstrate that measurement of pitting susceptibility using a higher surface area specimen provides a more conservative result than a standard low surface area specimen, which is of practical value where cost constraints preclude statistical analysis of data from multiple repeat tests.

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1. Introduction

Localised corrosion of corrosion resistant alloys (CRAs) is a major issue for the oil and gas industry and can arise as a result of inadequate material selection, unforeseen operating conditions or poor fabrication, e.g. sub-standard welding. The challenge is to identify whether an alloy will be susceptible to localised corrosion for the intended application and to be able to detect and monitor development of localised corrosion in the field, should it initiate. In many applications the localised corrosion rate of CRAs can be relatively high so that most often resistance to initiation is considered to be the primary requirement. In the oil and gas industry, the materials selection process is typically based on extensive stress corrosion cracking (SCC) test programmes, which are time consuming, expensive and lacking in fundamental scientific insight as they are based on simple pass/fail criteria associated with the observation of cracking. In applications in which localised corrosion acts as a precursor to cracking, e.g. SCC of duplex stainless steel in formation water environments, characterisation of the susceptibility of a material to localised corrosion using electrochemical test methods could provide a relatively quick and cost effective means of assessing the suitability of a material for a given environment.

The use of electrochemical techniques in the characterisation of localised corrosion of CRAs is well established at relatively low temperatures (<90 °C) and in relatively dilute solutions [1]. Measurement of pitting potential and repassivation potential is the most common method for ranking pitting corrosion resistance, with appropriate precautions to avoid interference by crevice corrosion (for example, using a flushed port cell [2]). The pitting potential refers to the potential at which an initiated pit stabilises and pit growth is sustained. In testing, the potential is scanned from some initial value and the current monitored until a sustained increase in current above that of the passive current or the noise level associated with metastable pitting events is observed. Reliable determination of the pitting potential from the polarisation curve as the value corresponding to the onset of that sustained current increase presents a challenge. To achieve consistency in the way in which the pitting potential is determined the relevant ISO committee adopted the approach of assigning the pitting potential to the potential at which a sustained increase in current density above a defined value (optionally $10 \, \mu A/cm^2$ or $100 \, \mu A/cm^2$) is achieved [3]. In this study we have used the $100 \, \mu A/cm^2$ criterion. However, to avoid misrepresenting the associated potential as the pitting potential we introduce a term E'_{c100} as the potential corresponding to that current value. While it is recognised that use of the E'_{c100} potential is an imperfect method that may lead to non-conservative results when the increase in current close to the pitting potential is not sufficiently abrupt, such

cases may be identified by the user and treated accordingly. The repassivation potential, E_{rp}, is defined as the potential at which the hysteresis loop in the reverse scan is closed.

Since the potential for onset of crevice corrosion is more negative than that for pitting corrosion, prevention of crevice corrosion during anodic polarisation is critical if the results of the test are to be valid. In the flushed port cell, this is achieved by pumping deionised water into the region between the specimen and its seal. However, the flushed port technique has a number of limitations:

(i) The specimen is not usually fully immersed in the test solution so temperature gradients may exist in tests above room temperature.
(ii) Dilution of the test solution close to the specimen surface can lead to non-conservative results.
(iii) At elevated temperature and pressure the use of a flushed port is experimentally challenging.
(iv) Its use at high chloride concentrations is hampered by the need to balance the test solution by pumping in doubly-concentrated solution, which often lies beyond the solubility limit for NaCl.

Attempts have been made to address some of these issues, such as the fully immersed flushed port cell developed by Yamazaki and Shibata [4,5], which overcomes limitation (i) above. The bent wire electrode configuration established by Stockert et al. [6] is a convenient way of circumventing the need for a flushed port altogether but is limited to nitrogen-purged environments due to the possibility of water-line attack under more aggressive conditions. Use of epoxy coatings is feasible if crevice corrosion between the specimen and the epoxy can be prevented; this may be achieved by passivating the material in nitric acid, applying the coating and then grinding to expose a well-defined area of non-passivated material [3]. However, the major limitation of this approach is the performance of the epoxy at elevated temperature.

In this paper we describe two experimental innovations, both of which represent a significant advance on standard techniques for anodic polarisation measurements. The first is the use of a high surface area rod specimen that is fully immersed in the test solution, overcoming limitation (i) above and reducing the number of tests required in situations where cost constraints prevent multiple repeat tests, for example with high temperature, high pressure autoclave tests. The second is the use of cooling rather than dilution to prevent crevice corrosion in tests at elevated temperature, which provides an elegant solution to limitations (ii) – (iv) and facilitates measurement of pitting and repassivation potential in representative oilfield environments.

The effect of a range of material and environmental variables on the pitting potential of CRAs has been well documented in the literature. Stable pit initiation is favoured on rougher surfaces due to the presence of occlusions which maintain an aggressive chemistry close to the surface of the metal. The pitting potential can be significantly affected by grinding, as witnessed by studies on the effect of grit size [7,8], grinding force/speed [9], grinding fluid [10] and surface composition [11]. Surface treatments such as pickling and passivation [12] and peening [13] have also been shown to influence resistance to pitting. In recent years there has been increasing interest in the effect of cold work on initiation and propagation of localised corrosion [14–16]. Pitting potential measurements may also be affected by scan rate [17] and local hydrodynamics [18] with the measured pitting potential tending to increase at higher scan rates and flow rates. In addition, the measured value is sensitive to the exposed surface area of the specimen [19,20], particularly for materials with a low density of inclusions, with the pitting potential tending to decrease with increasing specimen area. Thus, it should be recognised that the pitting potential is not an intrinsic property of the material but reflects all of these factors. This should be taken into account in any attempt to correlate the results of laboratory tests with predicted behaviour in service. A sufficient degree of conservatism is usually built into design codes and standards.

The commonly accepted method for statistical analysis of pitting potential measurements is to fit the data to a normal distribution and extrapolate to the low probability region to obtain a minimum pitting potential [3]. However, the choice of the low probability value is somewhat arbitrary and there is no obvious way to extrapolate the data to larger areas. More sophisticated statistical methods have been widely employed in the characterisation of pit propagation, e.g. in the prediction of pit depth distribution [21]. Maximum pit depth distributions have been determined using Type I (Gumbel) extreme maximum value statistics [22] and a generalised extreme value function for which no distribution type is assumed [23]. In contrast, efforts to apply extreme value statistics to the analysis of pitting potential data have been limited [24].

Here we demonstrate the use of Type I (Gumbel) extreme minimum value statistics in the analysis of E'_{c100} measurements. The key concept is the assumption that each measurement of pitting susceptibility is inherently the minimum value of a distribution of pitting susceptibilities across the specimen surface. The advantages of this approach are that it can be applied to non-normal distributions and it allows the use of an area scaling factor to extrapolate the results to larger areas.

2. Experimental

2.1. Materials

The material used in this study was a super 13 Cr martensitic stainless steel (S13Cr SS) typical of that used in oil and gas production, which was supplied in tubular form. The material composition is shown in Table 1. A range of disc and rod specimens were manufactured from the parent material for the electrochemical tests. Disc specimens of diameter 30 mm and thickness 10 mm were prepared for the standard Avesta cell tests and epoxy coated disc tests. Rod specimens of diameter 14 mm and length 110 mm were used in the high surface area flushed port cell tests. For the autoclave tests at elevated temperature, rod specimens of diameter 7.6 mm and length 380 mm were employed.

All specimens were received from the workshop with a surface finish of R_a = 0.1 μm as measured by surface profilometry. In order to generate a surface finish more representative of service conditions, the specimens were ground by hand to 600 grit before each test. The specimen preparation procedure was wet grinding to 240 grit and then 600 grit, rinsing in deionised water, cleaning in ethanol in an ultrasonic bath for 5 min, rinsing in acetone and then drying with compressed air.

2.2. Test cell configuration

Four different configurations of test cell were assessed in this work, as shown in Table 2. In the flushed port cell tests, deionised water was pumped around the crevice between the specimen and the seal in order to prevent crevice corrosion during anodic polarisation of the specimen. A filter paper ring was used to distribute the deionised water evenly around the edges of the O-ring seal. The flow rate of deionised water was adjusted to the minimum value required to prevent crevice corrosion (in the range 5–20 ml/h), as determined by preliminary tests. In order to balance any dilution of the test solution during the test, a solution of 7 wt% NaCl was pumped into the cell separately at the appropriate flow rate.