

ELECTROCHEMICAL NOISE GENERATION DURING STRESS (CORROSION CRACKING OF HIGH STRENGTH CARBON STEEL II MAXIMUM ENTROPY METHOD.

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ABSTRACT

The SCC processes of the high strength carbon steel alloy was investigated by the electrochemical noise generation during corrosion processes. The investigation was carried out under free corrosion potential in an acidified NaCl solution (3.5% NaCl + dil. H₂SO₄), poisoned with Na₂S (500ppm). The electrochemical noise was observed as spontaneous fluctuations of potential. The readings obtained were analysed using the maximum entropy method. The spectrum standard deviation and the roll-off slope are the measured parameters which appeared to give the clearest indication of the results. All the noise amplitudes generally increase with decreasing frequency and the power spectral density are inversely proportional to some power of the frequency thus indicating '1/f' or 'flicker' noise.

INTRODUCTION

Noise is a general term used to describe the fluctuating behaviour of a signal with respect to time. For the electrochemical corrosion, the process is stochastic, random in time and is the result of a series of transients associated with film breakdown or local corrosion events. Electrochemical noise has been defined (1-3) as the spontaneous fluctuation of the current passing through an interface (or of the potential) under potentiostatic (or galvanostatic)

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control. Electrochemical noise measurement is a new development in corrosion monitoring and in this case, the technique is non-perturbative. This phenomenon of electrochemical noise generation during corrosion processes has received considerable attention in recent years (4-8). The analysis of electrochemical noise is now known to give a useful information about the rate and nature of the chemical processes taking place at the electrodes. In this work, the electrochemical noise generated during the SCC of high strength carbon steel in a de-aerated acidified NaCl solution under free corrosion potential has been studied and the electrochemical noise spectra correlated with the progress of the stress corrosion test.

EXPERIMENTAL PROCEDURE

The quantovac spectrographic analysis gave the composition of the high strength carbon steel as: 0.95C, 0.35Si, 1.27Mn, 0.019S, 0.018P, 0.16Ni, 0.06Cr, 0.08Mo, 0.12V, 0.02Co, 0.002Ti, 0.028Nb, 0.23Cu, 0.05Al, 0.04Sn and 0.017Pb. The high strength carbon steel was cut into plates each 120mm long, 1mm thick and 10mm wide. The specimen preparation, involved three phases: heat treatment, grinding and polishing, and the preparation of specimen holders. The specimens were placed in the heat treatment furnace with an argon atmosphere. The furnace was heated to a temperature of 800°C and the specimens were held there for 2 hours. The specimens were then removed and immediately quenched in oil. They were removed from oil, drip dried and

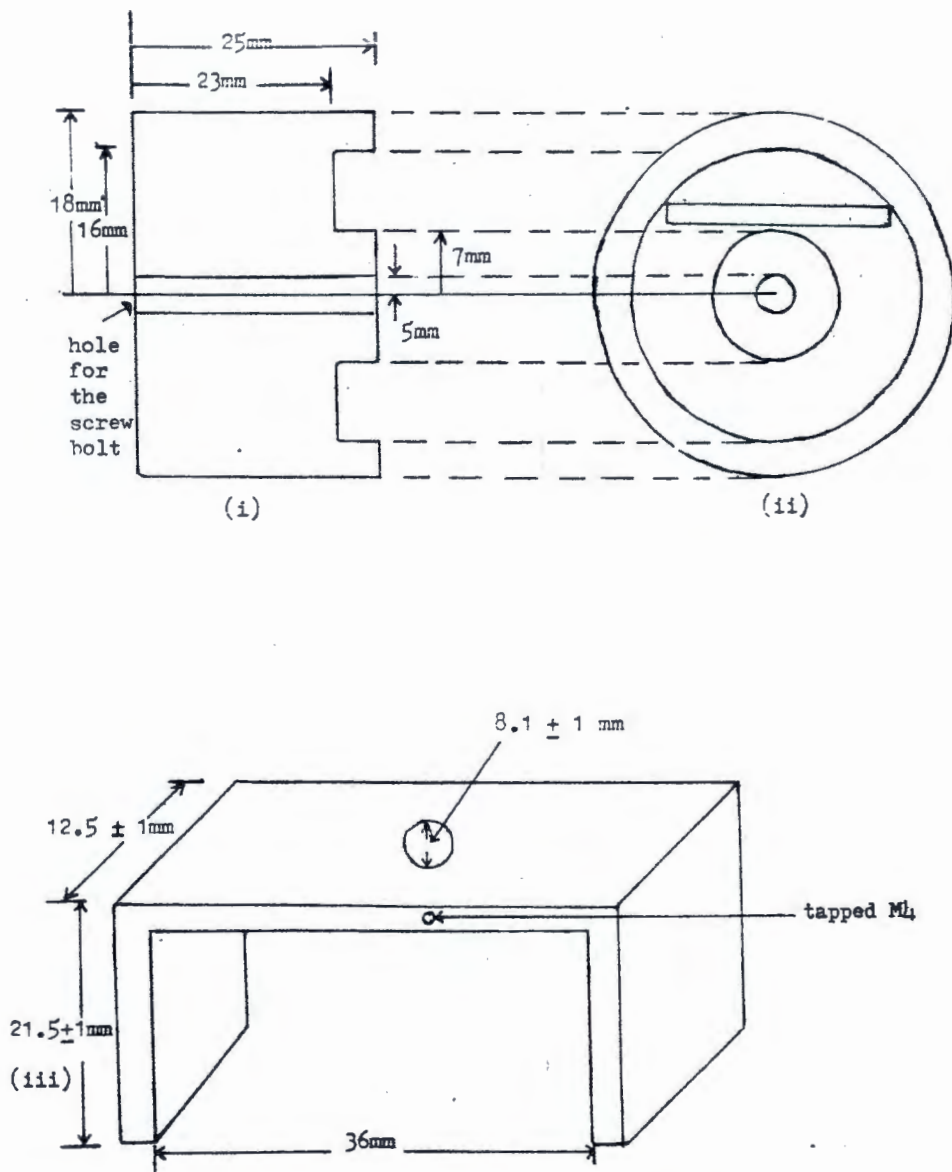


FIG.1 Specimen Holders (i) Design of Steel Ring Holder/Washer (ii) Front View of (i), (iii) Dial Gauge Holder - Standard U-Channel Section.

then placed back in the furnace and tempered by heating again, but to a temperature of 207°C, and held there for one hour before being removed. The specimens were ground by abrasive papers of up to 1200 grit. Before being used, each of the specimens was polished using 3µ and 1µ diamond polisher. The specimen holders, schematically shown in Fig. 1, were cut and machined to the required specifications. The specimen holder in Fig. 1 (i/ii) was used to hold the test specimen in the bowing position (bent plate), while Fig. 1 (iii) shows the dial gauge holder. The steel bolts used as part of the specimen holder were cut to 150 mm lengths and were 20mm in diameter.

The Analar grade NaCl was used to prepare 3.5% NaCl solution using distilled water. In addition, sodium sulphide (Na₂S) was added to the solution to a concentration of 500ppm. The solution was later acidified with dilute sulphuric acid (H₂SO₄) to a pH value of 2. The test specimens were stressed by bowing. A dial gauge was used for measuring the deflections as shown in Fig. 2. The steel bolt was clamped in a vice and the nuts were tightened until the desired deflection of the specimen was obtained. The central section of the specimen was deflected into the arc of a circle, and the stress in the outer fibre was therefore calculated by the formula.

$$S = \frac{4Etd}{l^2}$$

where:

- S = Stress in outer fibre
- E = Young's modulus
- d = distance from the outer fibre of the arc to the chord;
- t = thickness of the specimen
- l = length of the chord;

d was measured by means of a dial gauge reading to 0.001mm. The fixed legs of the dial gauge holder were 60mm apart. The zero of the gauge was determined on a piece of glass plate. Stresses of 50%, 45%, 40% and 35% of the yield stress, Y.S. (1137MPa) were made as needed. Some preliminary tests of time-to-failure were made under free

corrosion potential. A digital voltmeter and chart recorder were used for the potential monitoring. Nitrogen was continuously passed into the solution for deaeration. All the failure times were accurately observed visually. Monitoring by chart recorder also showed accurately the failure times.

The electrochemical noise measurements were made using a stress of 35% (796MPa) of the Y.S. for all the test specimens. The acidified and Na₂S poisoned NaCl solution was taken into a specially prepared rectangular tank and sealed. The solution was connected to a standard calomel reference electrode using a PVC tube (which served as the salt bridge). Nitrogen was passed into the solution for de-aeration. The bowed specimen was put partially immersed into the solution and hung from a clamp. The specimen and the standard calomel reference electrode were separately connected to a solartron 7055 digital voltmeter which measured the potentials. The digital voltmeter was connected to a Hewlett Packard HP85 desk-top computer which controls the voltmeter. The readings measured by the voltmeter were sent to computer and stored on tape. The readings obtained were analysed in groups of 1024 in order to construct a frequency spectrum from the time record. Maximum entropy method was the algorithm used. The spectral density curves obtained for all the data files for each particular specimen were standardised into a uniform scale and then plotted on a single plot. Curves of spectral density (i.e. noise amplitude/frequency) were made. Spectrum standard deviation was the second output obtained from the analysis. These were used to plot the spectrum standard deviation/time curves. Some tests were similarly carried out for the unstressed specimens. Some experiments were also performed in which the progress of the crack initiation and growth was followed by means of plastic replicas taken from the surface and subsequently examined in the scanning electron-microscope. All the tests were carried out at ambient temperature.

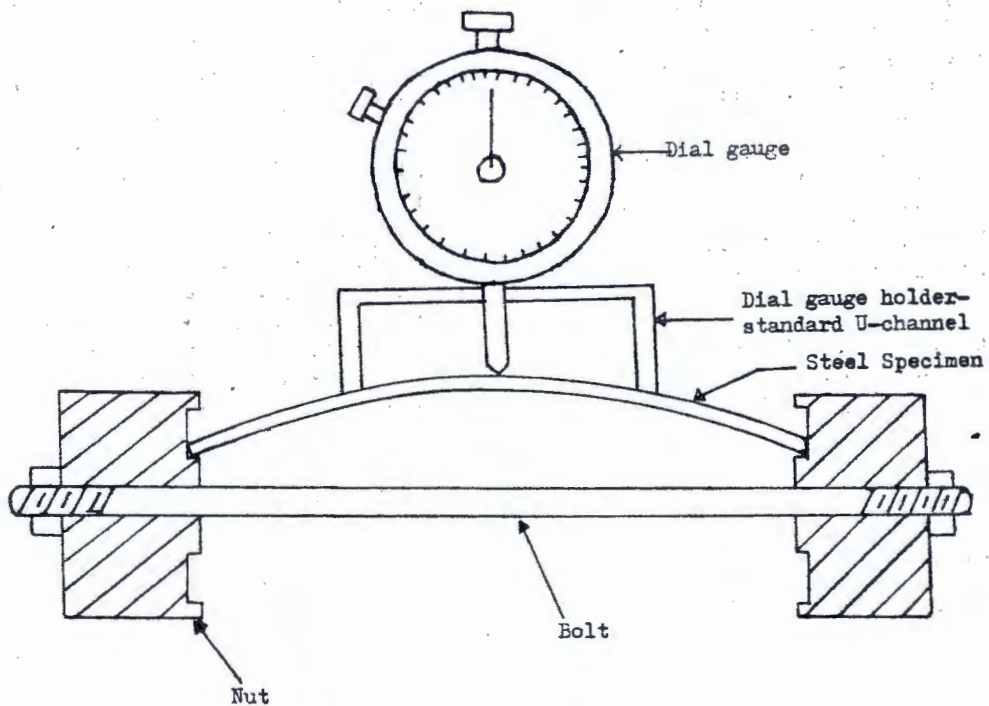


FIG. 2 Stressing of the High Strength Carbon Steel.

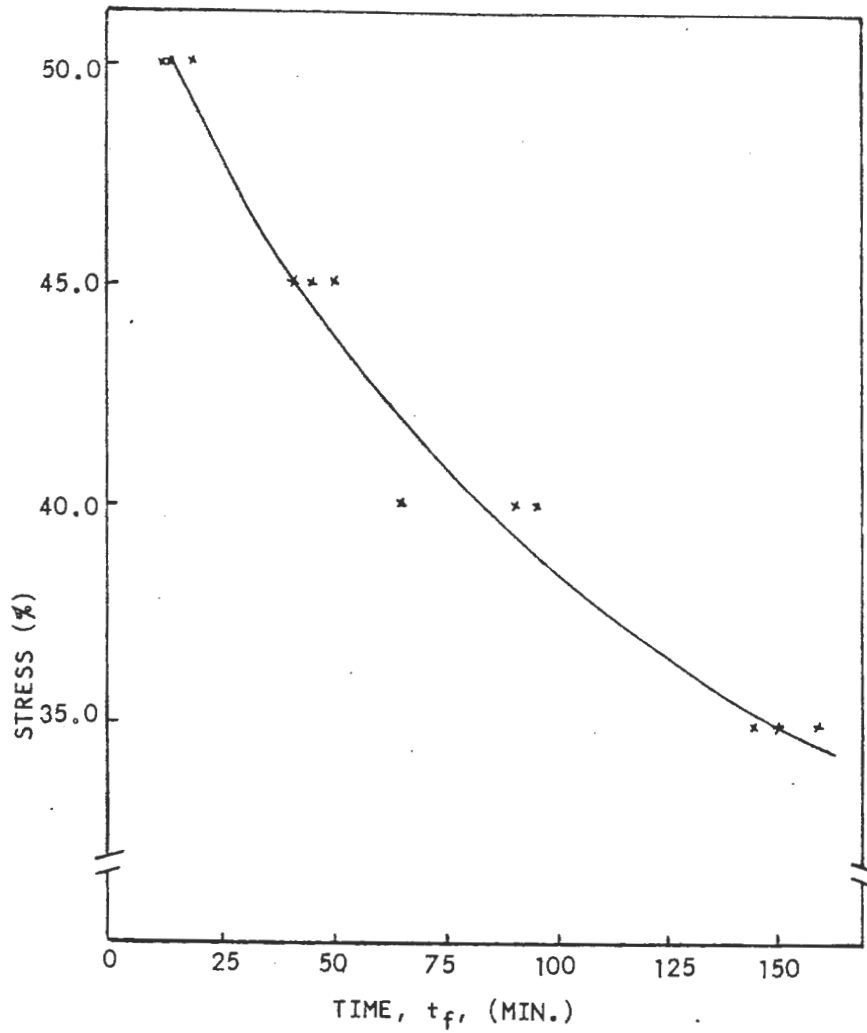


FIG. 3 Time to Failure V. Applied Stress - High Strength Steel.

EXPERIMENTAL RESULTS

The curve for the time-to-failure, Fig. 3, indicates that the failure time decreases with increase in the applied stress and vice-versa. In each case of a failure, a sudden brittle failure was observed. While the time-to-failure at 50% stress level (1137MPa) was about 13 minutes, it took 2½ hours for specimen at a stress level of 35% Y.S. (796MPa) to fail.

Electrochemical Noise Measurements

Spectral Density Curves (Noise Amplitude/Frequency)

The unstressed specimen curves, Fig. 6 show alternating spectral density curves and decreasing noise amplitudes with time as indicated by time record numbers. At low frequency, the spectral curves are distinctly separated but they are very close together at the higher frequency levels of 10 and 100 mHz. The cracking time record and hence the failure time for the stressed specimens, show the highest noise amplitudes at both the low and high frequency levels. The time-record, Fig. 4, at which the failure occurred is distinctly shown as time-record 8.

The standard deviation curve for the unstressed specimen, Fig. 5, rises to time record 3 and thereafter decreases with increase in time with some occasional slight fluctuations. In all the stressed specimen curves, the highest standard deviation peak shows the failure time. In Fig. 5, the highest standard deviation peak for the stressed specimen (270MPa) could be observed at exactly 2 hours 20 minutes from the start of the experiment.

In the spectral density curves, the time record figures are put in brackets, while the corresponding time (minutes) are written by the side(s).

In general, there was no indication of any change during the test, except for a large increase in standard deviation for the measurement period in which the final fracture occurred. In this period a single large transient could be seen on the time record and when this was eliminated from the analysis, even this period gave a spectrum which was similar to all of the earlier spectra. This steel was tempered to a very high strength and as far as could be determined, the failure occurred instantaneously, with only a single hydrogen embrittlement cracking event followed immediately by purely mechanical fast fracture. Since the corrosion process leading to hydrogen embrittlement is hydrogen generation, which should remain virtually constant throughout the test, the absence of detectable changes in the noise spectrum seems entirely reasonable.

The SEM micrographs made, show a lot of pit-like formations and evidence of anodic dissolution of the specimen's surface, Fig. 7. There was no evidence of crack prior to failure. The scanning electron microscope (SEM) examination of the fractured specimen's surface reveals, two different types of fractographic features in mixed form all over, Fig. 8. It is all a mixture of fibrous tearing as indicated by dimples (which are more) and cleavages which are characteristic of hydrogen embrittlement of steel. The fibrous tearing was likely to occur because of the very fast fracture of the specimen (sudden brittle failure).

DISCUSSION

Two major mechanisms of cracking most widely postulated to account for the stress corrosion cracking of high strength steels have been:

- (1) dissolution of the metal in the path of the crack, some times termed 'active path cracking, APC' and
- (2) hydrogen assisted cracking ('hydrogen embrittlement') from corrosion generated hydrogen (9).

The results obtained from the electrochemical noise measurements could probably be related to one of the above mechanisms (particularly the more favoured hydrogen embrittlement) in terms of the sources of noise generated, the behaviour of the noise as given by their spectral density curves, noise amplitudes, roll-off slopes and other characteristic parameters.

The general electrochemical noise behaviour as indicated by the curves of the spectral density/plateau noise amplitudes and the standard deviation peaks, presents a trend, where noise increases from the beginning in a manner corresponding to the degree of corrosion.

The increase in noise got to a peak after about one hour, then decreased for a period of about 20 minutes but not as low as at the beginning. At this level, the noise curve remained almost stationary for about another 40 minutes, though decreasing very slightly towards the end of the stationary period, after which the highest noise (amplitude) or the highest standard deviation peak was obtained. This corresponds with the time the sudden brittle crack or failure occurred (usually observed).

The trend discussed above can be divided into three phases of:

- i. - active general corrosion by metal dissolution
- ii. - stationary period
- iii. - metal brittle failure

These three phases can be schematically presented as shown in Fig. 9.

The spectrum of the unstressed alloy, Fig. 6, decayed with frequency, though the roll-off generally takes place at about 8 mHz. The noise amplitudes as indicated by the time record numbers of the spectral density curves are distinctly separated at the low frequency, thus indicating the occurrence of low frequency noise. These conform with the '1/f' or

'flicker' noise.

The rise in the noise amplitude from time record 1, (0-20 min.) to time-record 3 (40 min,) can be associated with general corrosion resulting from the specimen's dissolution in the aggressive environment.

This increase in noise amplitude gives increasing negative roll-off slopes of -11, -17 and -18 dB/decade respectively for the time records 1, 2 and 3 (40-mins.). From time record 4, (60 min.), the noise amplitudes decrease very slightly with time and show a slight decrease of negative roll-off slopes which are almost constant at -16dB/decade throughout. A plausible explanation for this decrease in noise amplitude is that the precipitation of corrosion products might have hindered partially the active corrosion of the specimen. In addition, there might be a decrease in the degree of corrosion because of increasing contamination of the test environment by the corrosion deposits, lessening the chemical reactivity. The spectrum standard deviation/time curve, Fig.5, corresponds with the spectral density curves and hence can be similarly used for this discussion.

All the stressed specimens, (as exemplified by Fig. 4), show similar characteristics as the unstressed specimen with respect to the type of noise and spectral density curves. Here also, the spectrum is inversely proportional to the frequency, exhibiting high noise amplitudes at the low frequency and thus indicating '1/f' or 'flicker' noise. However, the roll-off occurs at a lower frequency (2mHz) when compared with that of the unstressed specimen (8mHz), and the decay with frequency of the power spectral density is more defined. These might be due to more intense corrosion (anodic and cathodic reactions) of the stressed specimens.

Like the unstressed specimen, the continuous increase in the noise amplitude from time record 1 (0-20min.) to time record 4 (60 mins.) of the spectral density curves as in Fig. 4,

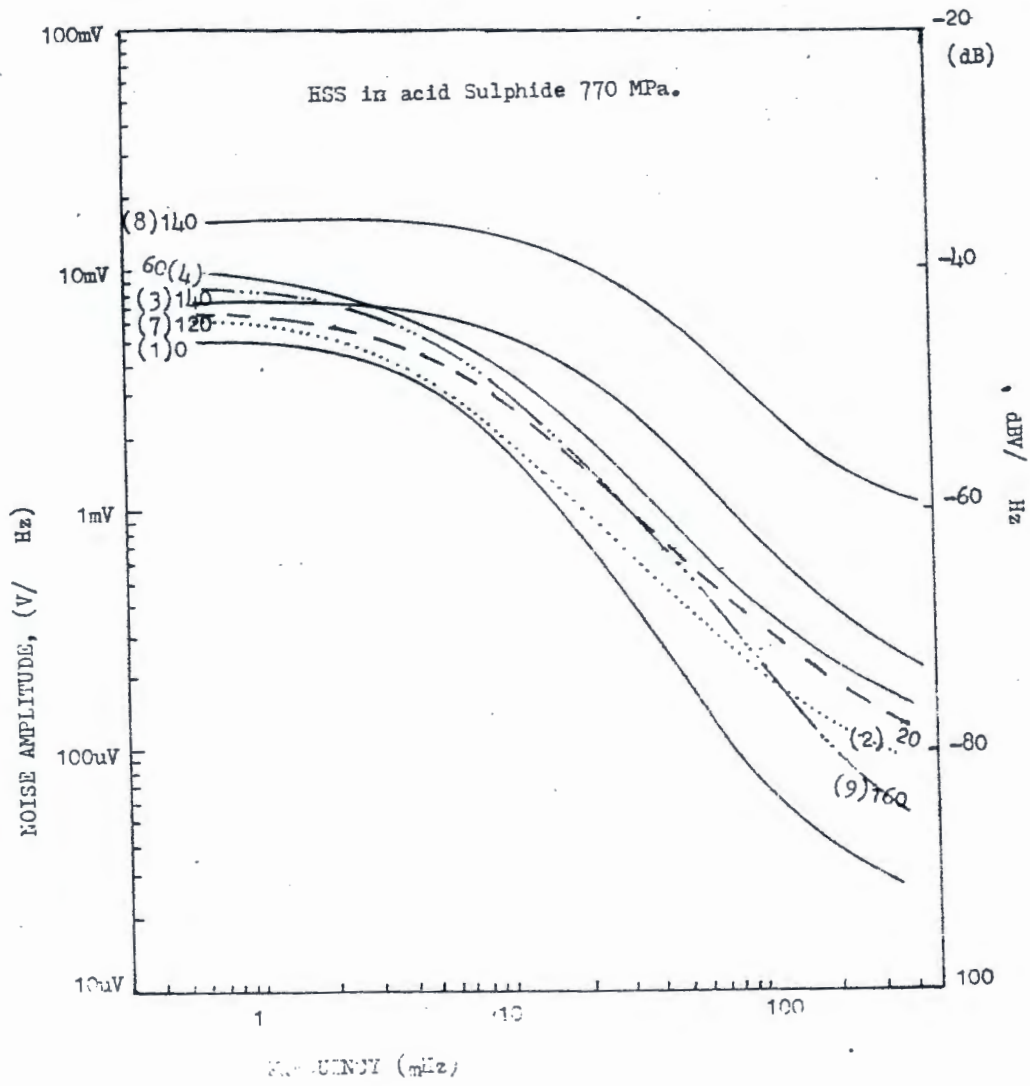


FIG.4 Selected Spectra - High Strength Steel, Stress 770 MPa.

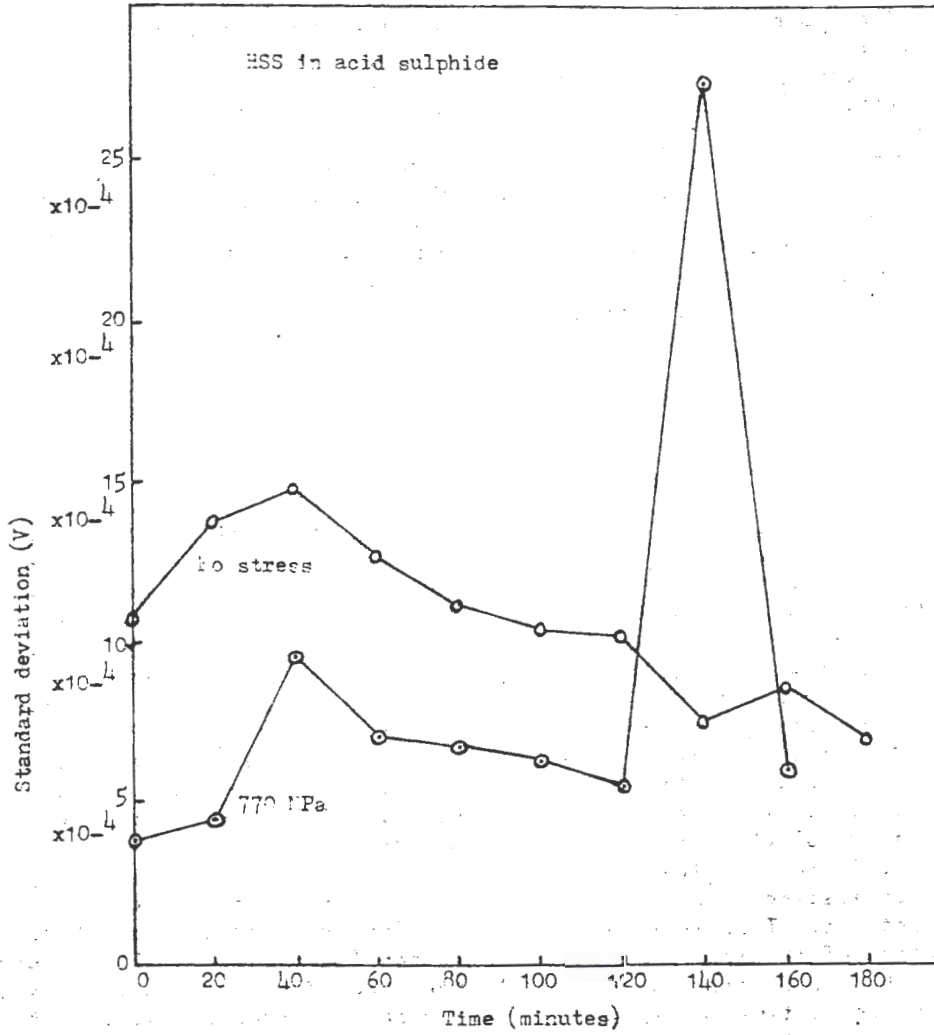


FIG. 5 Standard Deviation V. Time - High Strength Steel, Stress 770 MPa and unstressed.

might be due to general corrosion and/or dissolution of the specimen. A uniform noise amplitude was maintained at time record 5(80 min.) to 6(100 min.) with a slight decrease at time-record 7(120 min.) and this was observed to be the period of intense hydrogen activities-hydrogen evolution and probable absorption and adsorption.

The increasing noise amplitude from time record 1(0 min.) to time record 3(70 min.) gives decreasing negative roll-off slopes of -26, -9 and -17 dB/decade respectively. A trend of increasing corrosion corresponding to a decrease of negative roll-off slopes is shown here. From the time-record 4, constant roll-off slopes of -19 dB/decade were obtained for time-records 4(60 min.), 5(80 min.) and 6(100 min.) while a roll-off slope of -18 dB/decade was obtained for the spectral density curve of time record 7.

This period of an almost constant roll-off slopes and stationary curve may be associated with hydrogen embrittlement reactions as given above.

No change in the electrochemical noise behaviour was observed up to time record 7(120 mins.) for both the unstressed and the stressed specimens. A very distinct and incidentally the highest noise amplitude with a roll-off of -13dB/decade was obtained for the spectral density curve at time record 8, (140 mins., Fig. 4) where failure occurred as visually observed. This can be explained to be due to the fresh surface of the bare metal which in contact with bulk solution creates a potential spike manifesting as noise due to the anodic reactions. This results in metal dissolution of the fresh surface. It may thus be inferred that the increase in noise at time record 8 (140 min.) is solely due to a single transient caused by failure of this specimen. The observation that no change occurred in both stressed and unstressed specimens up to time record 7 probably indicates that the corrosion process was mainly by hydrogen embrittlement reactions.

The various SEM micrographs, such as in Fig. 7 made along with the noise measurements clearly show some of the processes occurring on the specimen's surface. They correlate with the curves made from the interrupted noise measurement to present a more practical evidence of the sources of noise and the degree of corrosive attack. This correlation is obtained despite the problem of reproducibility of results due to the repeated withdrawal of the specimen out of and immersion into the test solution for plastic replication monitoring. The micrographs show large anodic dissolution of the specimen's surface and the various pit-like formations. These, in conjunction with the observed hydrogen generation, would have probably caused the higher noise amplitudes and the more defined spectral curves of the stressed than the unstressed specimens even before the failure occurred. No crack on the specimens surface could be observed from the micrographs before the sudden brittle failure.

For the mechanisms of cracking, it was observed in this work that dissolution of the specimen occurred as evidenced by the SEM micrographs, and this was accompanied by the generation of hydrogen which might have been from the pits and other forms of localised corrosion which occurred when the NaCl solution was acidified with H_2SO_4 . No change of corrosion behaviour was observed between the unstressed and stressed specimens until failure occurred and no crack was observed before then.

There was a considerable period of stationary corrosion rate before the sudden failure. The SEM micrographs of the cracked surface showed mainly deep dimples and some cleavages. All these observations, i.e. corrosion processes and phenomena are consistent with the hydrogen embrittlement mechanism.

CONCLUSION

- (1) The stress corrosion cracking processes of the high strength carbon steel alloy can be monitored

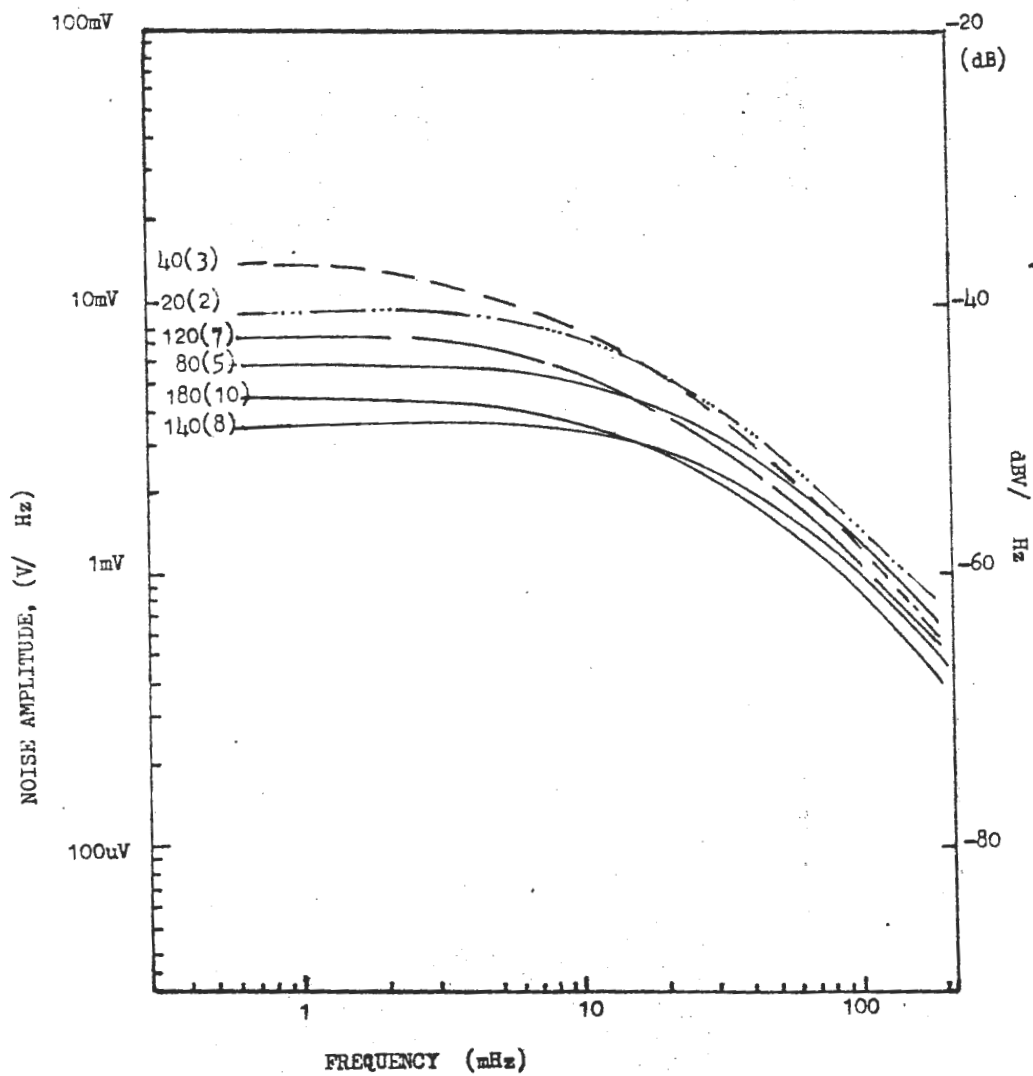


Fig. 6 Selected Spectra - High Strength Steel - No Stress.



Fig. 7. Corroded surface of the specimen in solution
- High strength steel, stress 770 MPa.

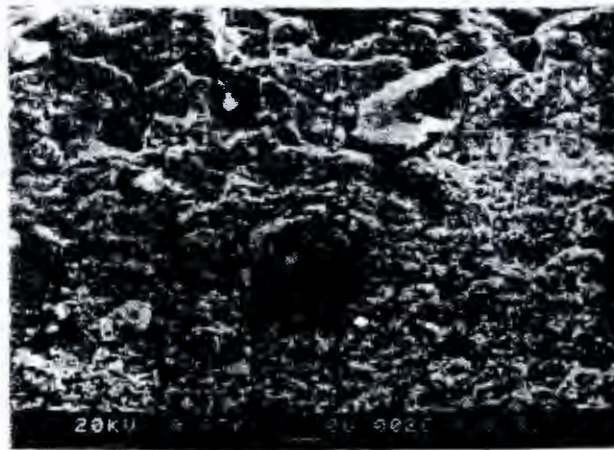


Fig. 8. Fractured surface of the High Strength Steel.

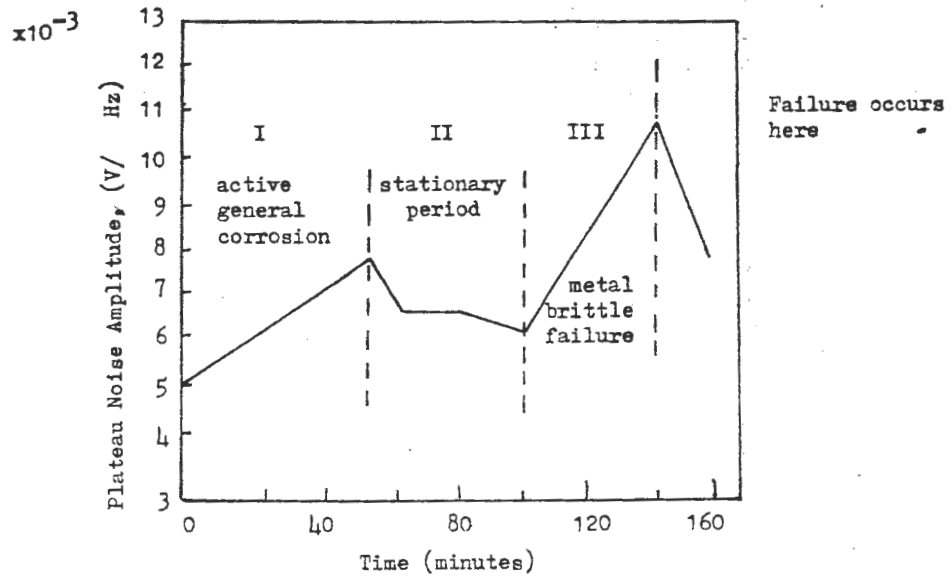


Fig. 9. Schematic representation of electrochemical noise behaviour of high strength carbon steel.

using the electrochemical noise measurement technique under free corrosion potential.

- (2) The high strength carbon steel failed in a sudden brittle manner showing a mixture of fibrous tearing and cleavage at the cracked surface.
- (3) The results obtained for the high strength carbon steel's corrosion behaviour are shown to be consistent with the hydrogen embrittlement mechanism.
- (4) The cracking of the specimen gave the highest noise amplitudes as described and explained in the text. The cracking failure is also indicated by the highest spectrum standard deviation peaks.
- (5) All the noise amplitudes generally increase with increasing frequency and the power spectral density are inversely proportional to some power of the frequency thus indicating '1/f' or 'flicker' noise.
- (6) Plastic replication monitoring of the specimen's surface can help in the elucidation of the mechanism for the stress corrosion cracking of alloys.

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