

Influence of applied stress on the critical potential for stress corrosion of carbon steels in nitrate solutions

A. ALDERISIO and B. BREVAGLIERI, Dipartimento ICMMPM, Università di Roma "La Sapienza", Rome, Italy.

Abstract

On a steel with 0.06%C, treated at 680°C for 5 h and cooled in the furnace, subjected to various loads, 40%, 60%, 80% and 100% of the yield strength, the critical potentials of stress-corrosion in a nitrate environment were singled out.

The potentials obtained, by means of the method of current-time transients, are: + 270 mV (40%), + 250 mV (60%); + 240 mV (80%) and + 140 mV (100%).

From these values, through a linear regression, it was possible to obtain a relationship between the applied loads and critical potentials of stress-corrosion, that is effective if applied only in the elastic range.

Riassunto

Influenza della tensione meccanica applicata sul potenziale critico di tensocorrosione di acciai al carbonio in soluzioni di nitrato

Su un acciaio allo 0,06%C, trattato a 680°C per 5 h e raffreddato in forno, sottoposto a carichi variabili, 40%, 60%, 80% e 100% del carico di snervamento, sono stati individuati i potenziali critici di tensocorrosione in ambiente nitrato.

I potenziali ottenuti, mediante il metodo dei transitori di corrente, sono: + 270 mV (40%), + 250 mV (60%), + 240 mV (80%) e + 140 mV (100%).

Da questi valori, attraverso una regressione lineare, è stato possibile ottenere una relazione tra i carichi applicati e i potenziali critici di tensocorrosione, che è valida se applicata solo in campo elastico.

Introduction

The initiation of stress corrosion requires the set-up of a certain critical balance between active and passive behaviours.

According to Parkins (1), the formation of cracks occurs only when the rate of formation and consequent exposure of new surfaces to an aggressive environment is definitely higher than the rate of repassivation.

If, in fact, the rate of repassivation is too high, conditions for bringing the material to the state of stress corrosion do not exist.

If, on the other hand, the repassivation is too slow, the chemical attack will produce pitting rather than cracking.

The parameters usually used to evaluate the susceptibility to stress corrosion are the threshold stress for crack initiation and the rate of crack propagation (2). Below the threshold stress, the surface film remains protective, because the rate of repair is higher than the rate of breakage induced by the applied stress.

At stress above the threshold level, the rate of film repair is less than the rate of breakage and creates conditions such that the locally exposed metal is dissolved, inducing crack growth.

The essential role of the load is its capacity to produce a rate of deformation such that, above the threshold stress, the rate at which the free metal is covered with the protective film is exceeded.

Parkins (3) found that no breakage occurred when a carbon steel was stressed and held at a non-rupturing potential for a certain time prior to polarising it in the critical potential range.

The explanation was that the rate of deformation was used-up to the point where it was below the level

needed to break the passivation film.

Rupture resulted from polarising in the critical range immediately after the application of the load, when the rate of deformation was still maintained.

It is important, therefore, to establish for each load condition a narrow range of working potential to be applied instantaneously, so that the stress corrosion occurs.

In fact, the new surfaces, formed by plastic deformation and consequent breaking of the passive film, because of work hardening, assume a free corrosion potential more active than the rest of the surface and become anodically polarised when they are kept potentiostatically at the initial corrosion potential (4,5).

The aim of the present work is to find a relationship between the applied load and the critical stress-corrosion potential. For such a potential, as mentioned above, there is a corresponding critical balance between active and passive behaviours (6).

The method used herein consists in recording amperometric curves at constant potentials within a certain range according to Parkin's method (1).

Such amperometric curves show the existence of a transitory stage characterised by continuous current oscillations, and of a second stage in which the current reaches a steady value (7).

Characteristic features of curves are the frequency of the oscillation and the duration of oscillating stage. Oscillations of small amplitude, high frequency and long duration provide situations not conducive to stress-corrosion.

On the other hand, when oscillating amplitudes ever greater and frequency ever lower are recorded, it can be assumed to stay close to the stress-corrosion potential to which, in critical zone, a steady-state high current corresponds (Fig. 1).

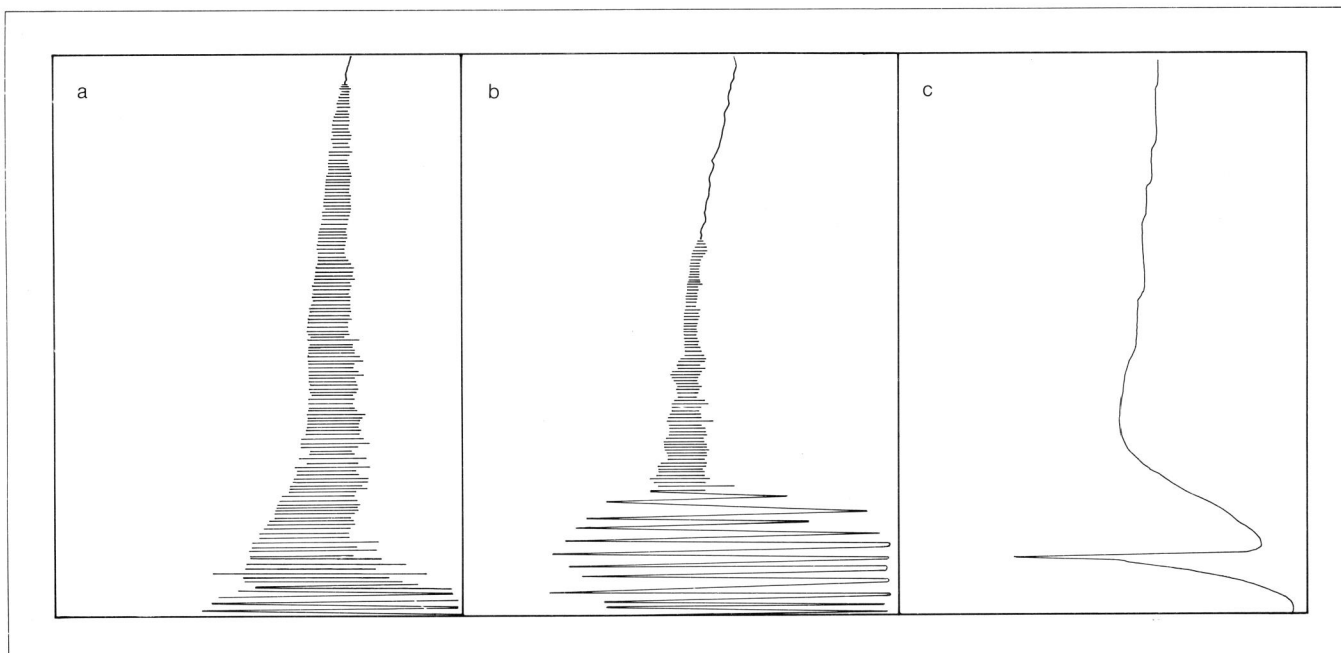


Fig. 1 - Typical amperometric curves:
a - no stress corrosion, b - various kinds of localised corrosion, c - stress corrosion.

Materials and apparatus

A mild steel, Fe42, with 0.06% C was used. This steel was subjected to a spheroidising annealing at 680°C for 5 h and then cooled in furnace.

Cylindrical specimens 120 mm long were taken, with a useful length of 40 mm, on which tensile tests after heat treatment gave the following results:

$$\sigma_s = 200 \text{ N/mm}^2, \sigma_r = 370 \text{ N/mm}^2$$

The area of the specimen exposed to the aggressive medium was 5.02 cm².

Before the experiment, the samples were finely grounded with SiC 1000, rinsed in distilled water, alcohol and dried with air.

The test solution was ammonium nitrate 3 N, prepared with pure reagent (Merck) and distilled water.

The cell used for electrochemical tests consisted of a closed cylindrical container with neoprene stopper, through which the sample passed. A helical platinum wire served as counter-electrode and a saturated calomel electrode was inserted as for reference.

A solution was thermostatically controlled at 70 ± 0.5 °C with an electric mantle controlled by a mercury contact thermometer.

The apparatus used for the electro-chemical tests was a Corrograph 561/B by Amel.

The specimens, after every electro-chemical experiment of 4 h duration, were cut along the

longitudinal section and examined by Neophot 2 microscope.

Experimental results

On the Fe42 steel, potentiodynamic curves were identified for two scanning rates (30 mV/min and 1200 mV/min) under loads equal to 40%, 60%, 80% and 100% of the yield strength (Fig. 2).

Looking at Fig. 2a, for the 40% test, a potential range from + 250 mV to – 280 mV was considered.

Amperometric curves were plotted for this range.

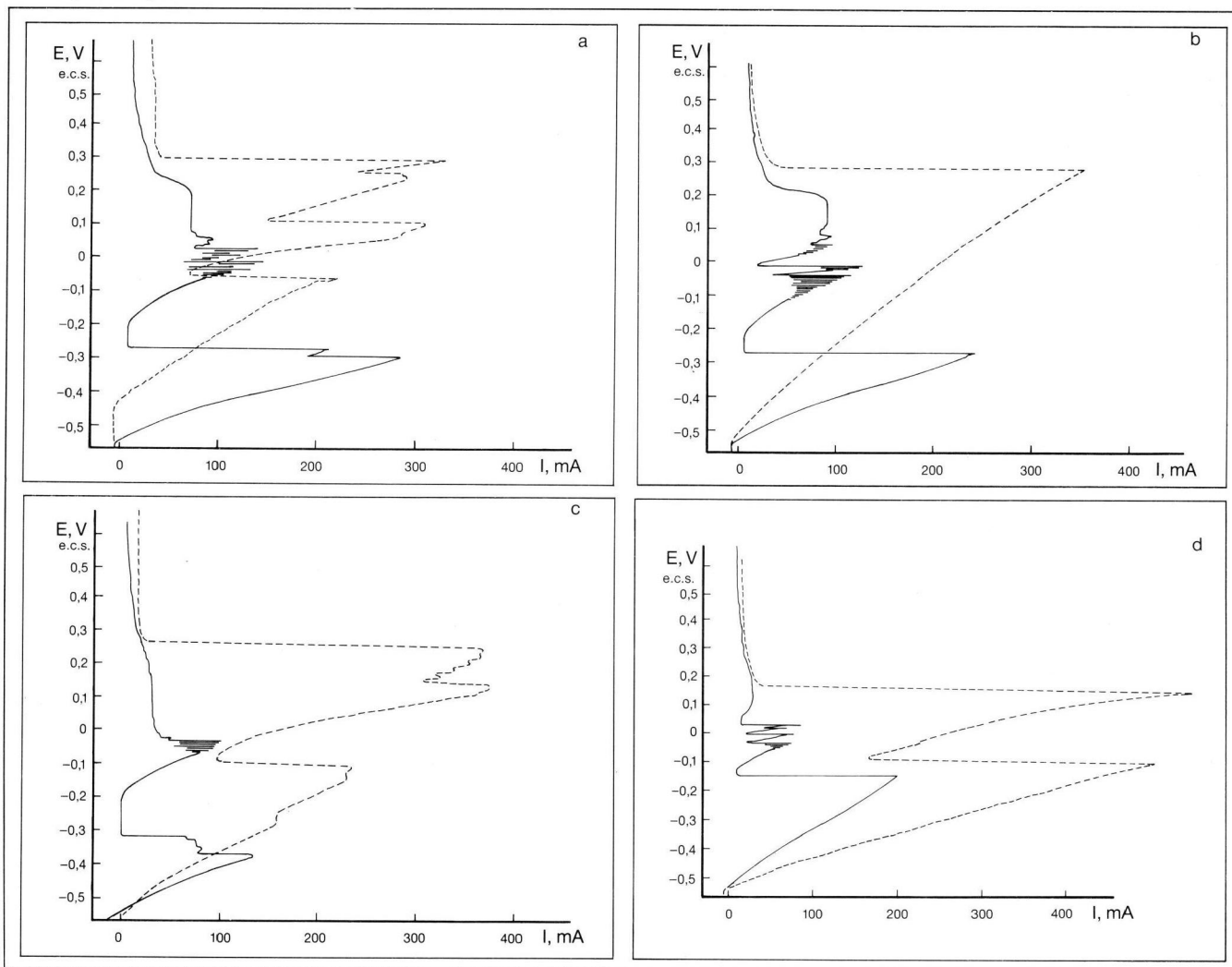
Fig. 3a presents the amperometric curve and the relative micrograph at the critical stress-corrosion potential of + 270 mV.

Looking at Fig. 2b, with loads equal to 60%, a critical potential range for stress corrosion was identified between + 230 and + 260 mV, and in Fig. 3b the amperometric curve is shown at + 250 mV, with the relative micrograph.

Looking at Fig. 2c, for 80% loads a critical potential range was identified between + 230 and + 250 mV, and Fig. 3c shows the micrograph made at the critical stress-corrosion potential of + 240 mV.

Looking at Fig. 2d, for loads equal to 100%, a critical potential range between + 130 mV and + 160 mV was identified, and the relative amperometric curve drawn. Fig. 3d gives the amperometric curve for + 140 mV and the relative micrograph.

Fig. 2 - Potentiodynamic curves at different scanning rates for various applied loads. a - 40% of yield strength, b - 60% of yield strength, c - 80% of yield strength, d - 100% of yield strength.



All the curves in Fig. 3 have the common characteristic of being the most suitable to represent the maximum stress-corrosion conditions (compare with Fig. 1). Furthermore, they are drawn for loads equal to 90%, 30% and 20% of the yield strength amperometric curves, which denote stress-corrosion phenomena for critical potentials of + 230 mV, + 280 mV and + 285 mV, respectively.

Discussion of results

Observing the results obtained by recording the potentiodynamic curves plotted in Fig. 2, we note that a rapidly-stressed specimen shows a shifting of the passivation potential (E_p) towards the active zone as a function of the applied load, since rupture of the passivation film creates, at the crack tip, free surfaces

that have lower polarisation potential. The passivation potential passes from a value of + 300 mV for the potentiodynamic curve at high scanning rate relative to specimens with 40% loads at a value of + 170 mV for a 100% load.

From the amperometric curves (Fig. 3) obtained at potentials of + 270 mV (40%), + 250 mV (60%), + 240 mV (80%) and + 140 mV (100%), we note a rapid attainment of constant current conditions, that provide for establishing of a stress-corrosion process confirmed by metallographic observation.

From the whole of these values with the methods of linear regression it is possible to obtain a relation between the applied stress and the stress-corrosion potentials:

$$E_{cr} = 300 - 77.14 \frac{\sigma}{\sigma_s}$$

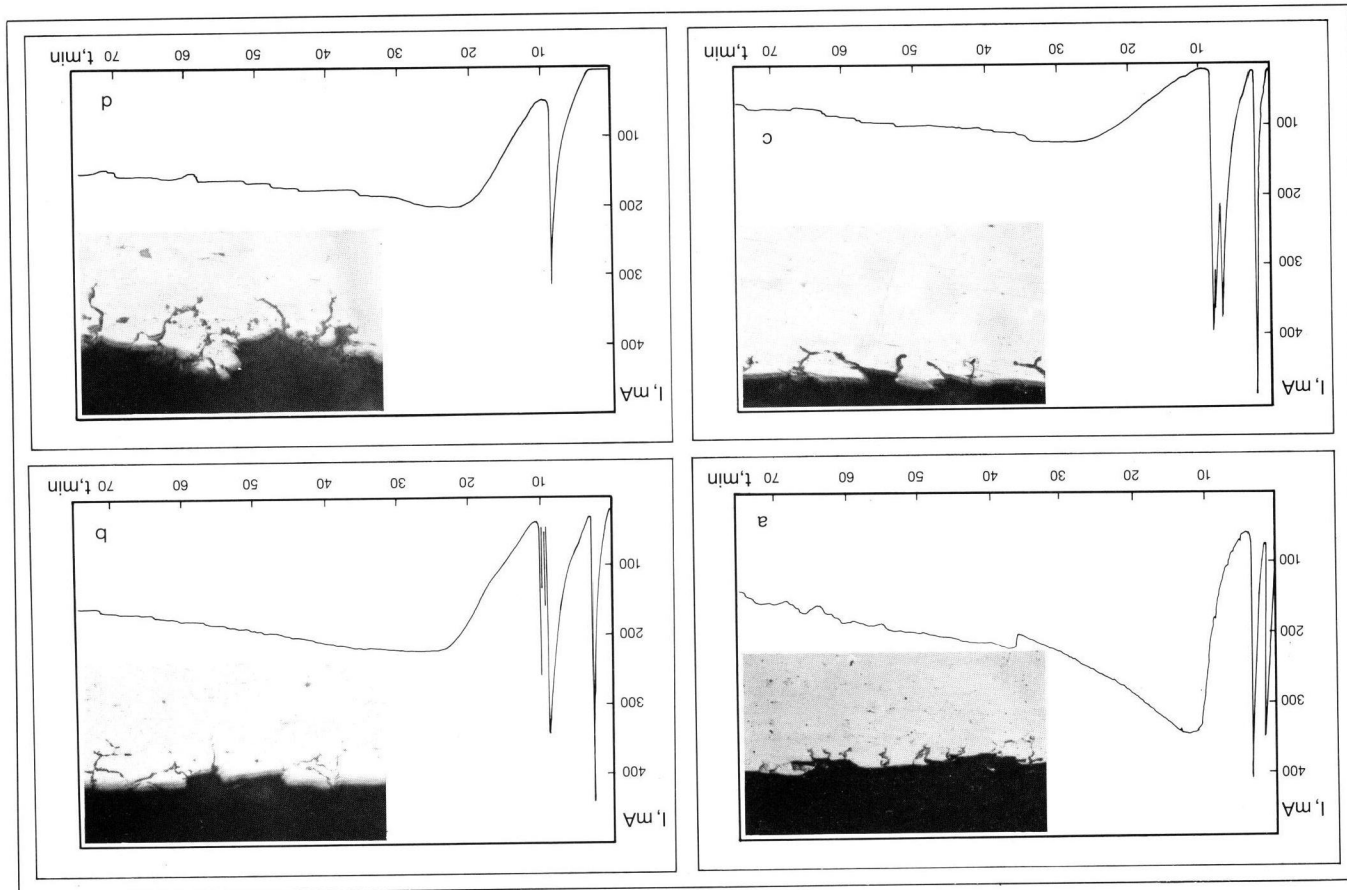


Fig. 3 - Amperometric curves and relative micrographs ($\times 200$).
a - + 270 mV, b - + 250 mV, c - + 240 mV, d - + 140 mV.

The critical potential value at 100% does not follow this rule. In fact, a theoretical value of + 233 mV corresponds to a much lower experimental value, + 140 mV. On the other hand, amperometric tests made at a load equal to 90% have provided, for the critical potential of stress corrosion, a value of + 230 mV, comparable with the theoretical value, which confirms that, for a deformation close to 100%, the above rule is still effective. This can be explained by the fact that when the yield point is reached — the point that determines the initiation of plastic deformation, or probably values above this — a marked increase in the deformation also occurs for small increases in the load, and the material will be subjected to structural variations and various mechanical properties in consequence of the hardening process. From the electro-chemical viewpoint, this corresponds to a significant negative shifting of the corrosion potential E_{corr} (8), and consequently of a strong increase in anodic current in the active-passive range.

The interdependence of applied load, critical potential and anodic current that results from a deformation, is therefore effective only when the specimen is kept in the elastic range (9). On the contrary, there will be a significant increase in anodic current and a significant denobilising of the potential E_p when the elastic limit is definitely exceeded, with consequent plastic deformation (Fig. 2). In fact, the decrease of resistance to reaction of the process of attack is due to the structural transformations that can occur in the materials during the growth of the defects and, in particular, to the increase in active centres characterised by low energy for anodic dissolution. Once the load-critical potential relationship for the particular system of metal and environment is found, it is also possible to single-out the threshold load for the corresponding critical potential. In fact, applying decreasing loads to the respective critical potentials, obtained with the above relationship, we can notice, from the course of the amperometric curves, whether stress-corrosion conditions are still present.

For loads equal to 20% and at the critical potential corresponding to + 285 mV, the amperometric curve is still the typical one for stress-corrosion conditions. The micrograph in Fig. 4 confirms this phenomenon. On the other hand, the specimen subjected to the same load and at an uncontrolled potential shows on its surfaces generalised corrosion — not selective. In these conditions the threshold stress is reached for the highest loads.

For loads lower than 20% and at controlled critical potentials, the amperometric curves record much lower current intensity values in the static phase, and the surface of the specimen is passive.

For this particular environment and for controlled critical potentials, there is therefore a fixed threshold stress equal to 40.7 N/mm^2 , a value comparable with that obtained by other authors under similar experimental conditions (10).

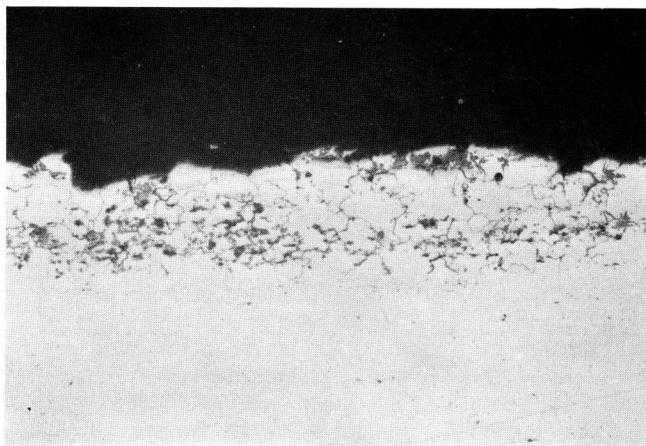


Fig. 4. Micrograph (x 200). 20% of yield strength at + 285 mV.

Conclusions

For the particular system of our study, a specimen subjected to constant stress showed:

- a) negative shifting of the corrosion potential (E_{corr});
- b) in the elastic range, a proportionality between applied stress and stress-corrosion critical potential;
- c) in the plastic range, a significant increase in anodic current and denobilisation of the potential E_p .

From the results achieved it is possible to obtain the threshold load for a corresponding critical potential; at an uncontrolled potential the threshold stress is reached, on the other hand, at higher loads.

REFERENCES

- (1) Parkins, R.N. *Corr. Sci.*, **20** (1980), 147.
- (2) Parkins, R.N. *Mat. Performance*, **24** (8) (1985), 9.
- (3) Parkins, R.N., and B.S. Greenwell. *Metal Sci.*, **11** (1977), 405.
- (4) Jones, D.A., C.D. Kim, and B.E. Wilde. *Corrosion*, **33** (2) (1977), 50.
- (5) Jones, D.A. *Met. Trans. A*, **16A** (1985), 1133.
- (6) Hurst, P., D.A. Appleton, P. Banks, and A.S. Raffel. *Corr. Sci.*, **25** (8/9) (1985), 651.
- (7) Alderisio, A., A. Borruto, and B. Brevaglieri. *Met. Ital.* (1986), in press.
- (8) Narayan, R., A. Kumar, and K.P. Singh. *Corr. Sci.*, **25** (6) (1985), 449.
- (9) France, W.D. *Corrosion*, **26** (5) (1970), 189.
- (10) Parkins, R.N., and R. Usher. *Proceed. of the First International Congress on Metallic Corrosion*. Butterworth Publishing Co., London, 1961, pp. 289.