

Review of surface factors in stress corrosion cracking of alloys

G. BOMBARA, Industrial Consultant, Rome, Italy.

Abstract

From morphological observations of typical cracks in a susceptible system of wide practical interest, a number of distinctive features is pointed out and a comprehensive definition drawn for stress-corrosion cracking. Electrochemical mechanisms of crack nucleation at passive or relatively inert surfaces and subsequent subcritical propagation of nucleated cracks are outlined according to the most accepted models. Besides the number of surface factors involved in both stages, special theoretical consideration is given to the direct role played by surface energy in a growing crack. This is in relation to the highly active state of the metal at the crack tip (i.e. high tendency to release surface atoms) in front of the passive state of side surfaces. In the light of the mechanisms outlined, basic techniques are described for the experimental study of stress-corrosion cracking susceptibility.

Riassunto

Ruolo dei fattori di superficie nella tensocorrosione delle leghe metalliche

Semplici osservazioni morfologiche su cricche prodotte in un sistema metallo/ambiente tipicamente suscettibile consentono di evidenziare una gamma di caratteristiche distintive e dare una definizione esatta e completa della cricatura per tensocorrosione.

In accordo con i modelli più accettati, vengono delineati i meccanismi elettrochimici di nucleazione di cricca, sempre implicanti superfici passive o relativamente inerti, e di conseguente propagazione subcritica della cricca nucleata. Tra i vari fattori di superficie in gioco in entrambi gli stadi viene prospettato il possibile ruolo diretto dell'energia superficiale metallo/mezzo all'interno della cricca avanzante. Ciò in rapporto allo stato estremamente attivo del metallo all'apice della cricca, con conseguente elevata tendenza a cedere atomi superficiali, contro lo stato passivo o inerte delle superfici laterali della cricca.

In diretta correlazione con i meccanismi, vengono descritte le tecniche sperimentali più efficaci per la valutazione e lo studio della suscettibilità alla cricatura per tensocorrosione.

Introduction

In spite of the enormous amount of relevant investigative work so far carried out, environmental stress cracking of metallic materials is still a major subject of theoretical and experimental research in such areas as elementary mechanisms and models, determining and influential factors, practical preventive measures, and methods of testing, studying and monitoring.

An essential feature of stress-corrosion cracking is the multidisciplinary knowledge required for a serious approach, even to a well specified system consisting of a material with known composition and structure, a physico-chemically characterized environment and a mechanically defined stress condition. This implies a cultural and instrumental complexity of any experimental set, a wide dispersion of theoretical and operative optics and even ideological conflicts among such different competences involved as those of electrochemists, corrosion researchers, mechanicians and metallurgists. A final complication is the natural propensity of most experienced research people to calculate and propose mechanical models of general value, which tend to be incompatible with the intrinsic complexity and variety of chemical, electrochemical, mechanical, geometrical and metallurgical aspects involved.

As a consequence, the subject of stress-corrosion cracking is quite difficult to treat according to an organic and unitary logic. Instead, the available knowledge can be reviewed through less contentious phenomenological evidence, apparent relationships and mechanistic features.

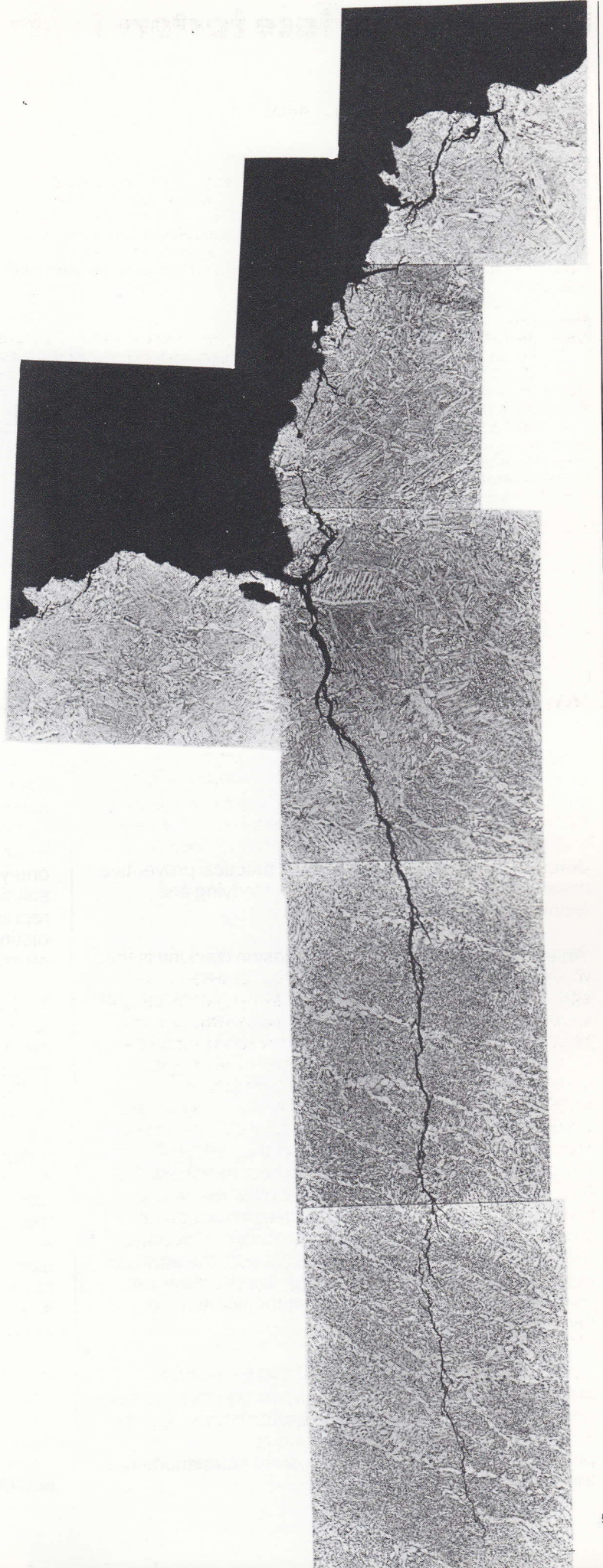
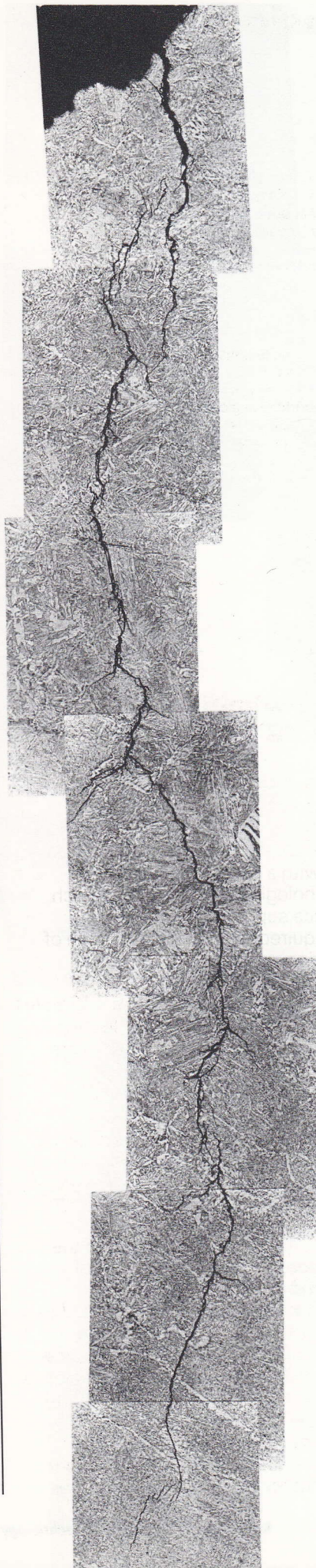
Morphology and definition of stress-corrosion cracking

For the sake of concreteness, straightforward reference can be made to a few micrographic examples, shown in Figures 1 to 4, of very typical cracks formed in a low-alloy steel pressure vessel in one-year's operation with a hot alkaline carbonate solution. A plain morphological examination of such representative evidence supplies almost all the distinctive features required for a sound definition of stress corrosion cracking.

- Cracking is drastically brittle in that it does not imply any macroscopic plastic deformation in the surrounding metal mass. This means that gross stress levels are definitely below the material yield strength.
- Cracking is definitely multiple, that is, a number of similar cracks is apparent in the affected material. This denotes a general susceptibility somewhat independent of the stress level as well as the microstructure. In the latter regard, cracks are present either in the base material or the weld metal, or in the thermally affected zone.
- All the cracks appear to have been initiated at the external exposed surface, with some evidence of nucleation from localized corrosion penetrations.
- Every crack is widely branched along its route. This denotes that, within cracks too, there is a general susceptibility relatively independent of the stress level.
- The ratio of metal surface area to electrolyte volume within a crack is greater by several orders of magnitude than for external surfaces. This implies an extremely high chemical polarizability due to metal ions concentration in the case of anodic dissolution and to depletion of oxygen or other oxidizing species in the

Fig. 1 - Stress-corrosion cracking in a low-alloy steel: Typical micrograph (50X)

Fig. 2 - Stress-corrosion cracking in a low-alloy steel: Typical micrograph (100X)



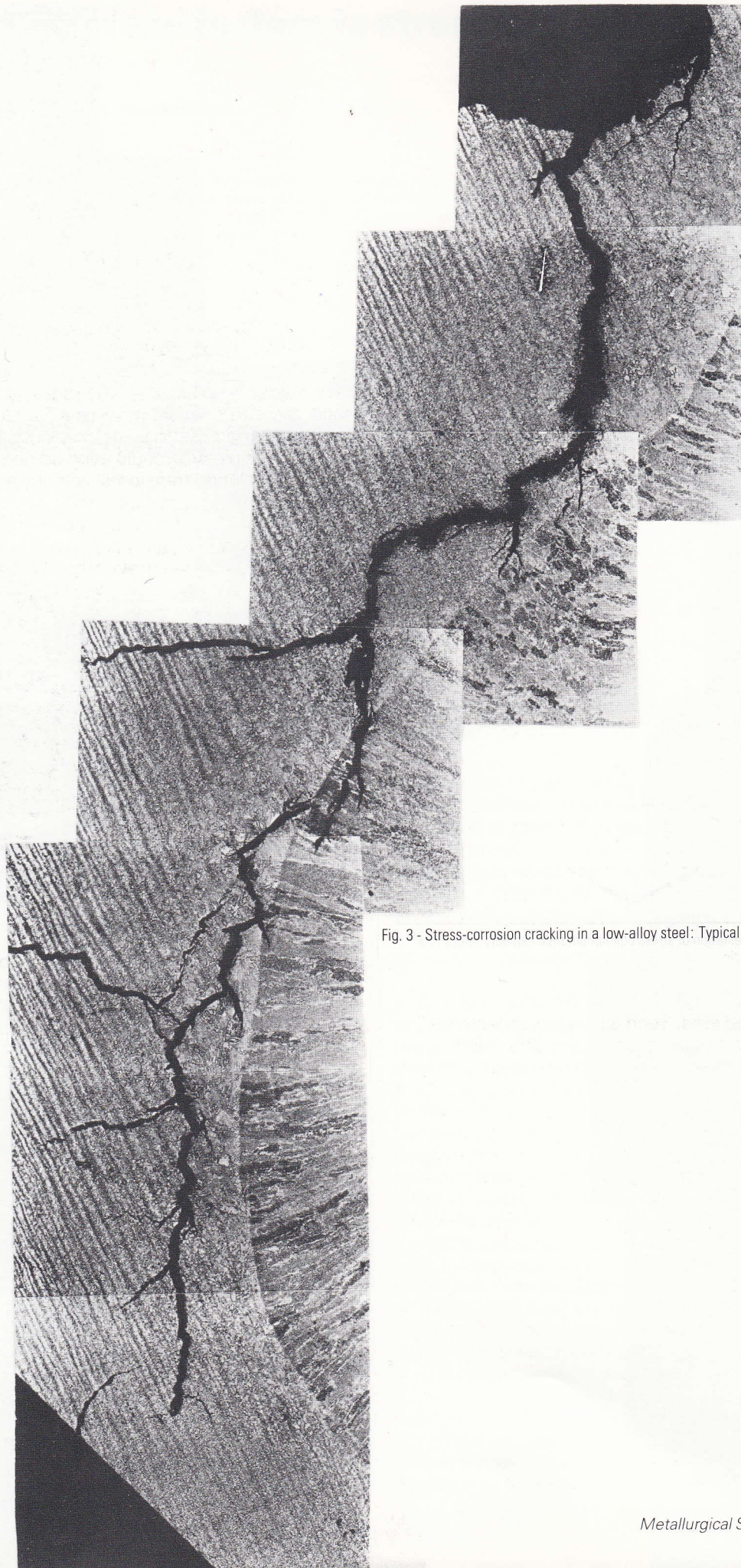


Fig. 3 - Stress-corrosion cracking in a low-alloy steel: Typical micrograph (100X).

Fig. 4 - Stress-corrosion cracking in a low-alloy steel: Typical micrograph (200X).



case of oxide filming reactions.

- The extreme occlusivity of a well-grown crack leads us to infer that chemical and electrochemical internal conditions, beyond a certain stage of growth, can be quite different from those at external surfaces in contact with free solution.
- Considering the relatively long time required for crack growth, the rate of corrosive consumption at the crack sides appears to be quite negligible, if not zero, with respect to the rate of crack growth. In other words, crack side surfaces are relatively passive or inactive in front of the apparent activity at the crack tip.
- From the point of view of fracture mechanics, aiming at the definition of a threshold value of stress intensity (K_{Isc}) for crack extension in a pre-cracked system, all the cracks appear to be largely subcritical. This means that the fracture mechanics approach by the well-known curves " crack growth rate vs stress intensity " (Fig. 5), though most useful in constructional design for establishing the size of propagable defects is not suitable at all for studying the very initiation and the actually subcritical growth of stress-corrosion cracking in which cracks nucleate at initially flat surfaces (i.e. $K_I = 0$) and grow up, to a large extent, at stress intensity levels at crack tips that are well below any critical value given by fracture mechanics (i.e. $K_I \ll K_{Isc}$). However, the sphere of proper subcritical propagation reduces sharply with increase in the yield strength of the materials involved. This is the reason why fracture mechanics is very suitable for studying the behaviour of high — and ultra-high — strength alloys, for which the specific influence of the exposure medium also strongly reduces, so that a unique value of K_{Isc} , as determined in sea water or simply sodium chloride solution, is representative of many environments of practical interest.
- With reference also to the great number of field and laboratory experiences available, susceptibility to stress-corrosion cracking is typical of systems characterized by a proper passivity or, at least, a relative inactivity of the chemical environment to which it is exposed. This means that stress-corrosion cracking conditions are also largely subcritical in respect to corrosion.

On the basis of the above observations, the fracture stability/instability of a class of materials whose strength is modifiable by thermal treatment, or by low-alloying, can be aptly described by diagrams such as that shown in Fig. 6 for a martensitic low-alloy steel⁽¹⁾ as a function of yield strength and stress intensity, where three distinct regions are outlined:

- a region of purely mechanical crack propagation to rupture;
- a region of environment-assisted crack propagation;
- a region of environment-induced subcritical

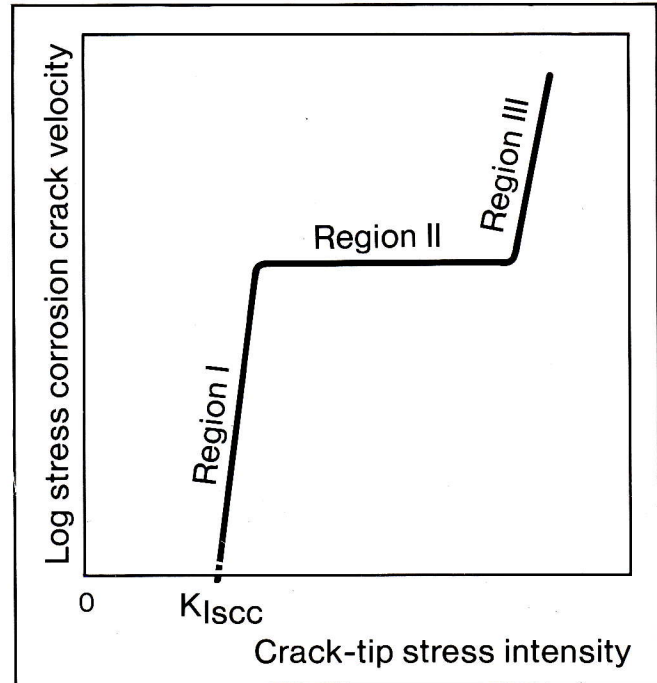
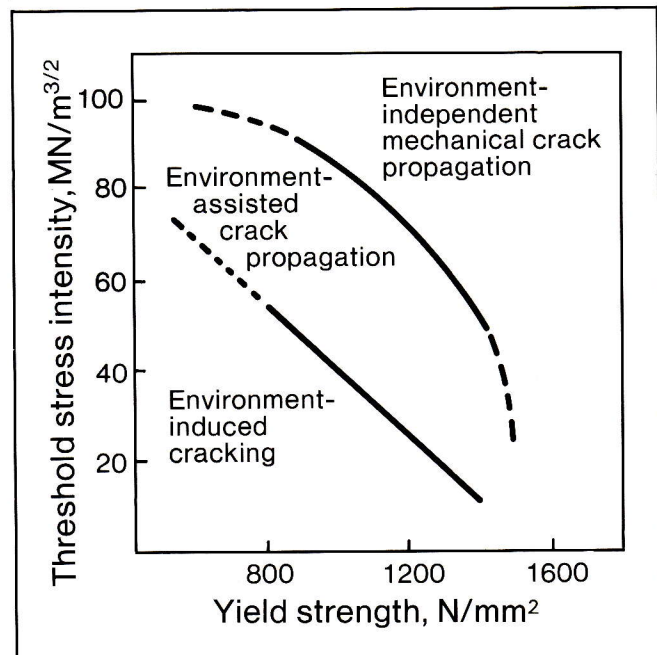


Fig. 5 - Schematic representation of the influence of stress intensity on stress-corrosion crack velocity.

Fig. 6 - Environmental effects on stress cracking and crack growth in a AISI 4340 plate⁽¹⁾.



cracking i.e. stress corrosion cracking proper. The last can be exactly defined as "environment-induced surface nucleation and brittle propagation of cracks in a stressed material under conditions definitely subcritical for both corrosion and fracture mechanics".

Electro-chemical aspects in crack nucleation

Numberless experimental examples of stress-corrosion cracking lead to point out the sequential occurrence of the following stages:

1. gross passivity of external metal surfaces;
2. localized corrosion penetrations;
3. evolution of some most penetrating geometries to wedge-shaped micronotches and eventually actual cracks.

As illustrated in Fig. 7 with specific regard to pitting, the relative rates and the directional distribution of metal dissolution are quite different in the three stages. While a zero or very low and uniform consumption rate pertains to the passive surface, high dissolution rates result at localized breakdowns in the passive coverage, with a multidirectional distribution in the case of shallow pits (Fig. 7b) and a preferential direction in the case of penetrating pits (Fig. 7c). Eventually, in order that the geometry of a nucleated crack may be retained, the dissolution rate at the crack tip must be higher by orders of magnitude than that at any other exposed surface, including the crack sides (Fig. 7d). This supports the inference drawn from morphological observations that stress-corrosion cracking must be looked for primarily in metal-environment systems displaying a definite active-passive behaviour electrochemically characterized by anodic polarization curves as that schematised in Fig. 8 for the most comprehensive case of existence of two transition zones, i.e. potential ranges where the passive state shows kinetic instability.

A first zone of susceptibility is the low-potential transition range in the polarization curve where the passivating film is not complete or perfect, and coverage defects can induce localized attacks of the type generally known as electrolytic crevice corrosion.⁽²⁾ Beyond the intrinsic defectiveness of this transitional filmed state with consequent proneness to localized corrosion, a critical feature lies in the fact that, in the presence of stress, any plastic deformation in the metal substrate would give rise to metal-oxide disbonding and oxide-film ruptures, i.e. active interstices leading to sharply localized penetrations (Figs. 9 and 10) at which cracks can nucleate.⁽³⁾

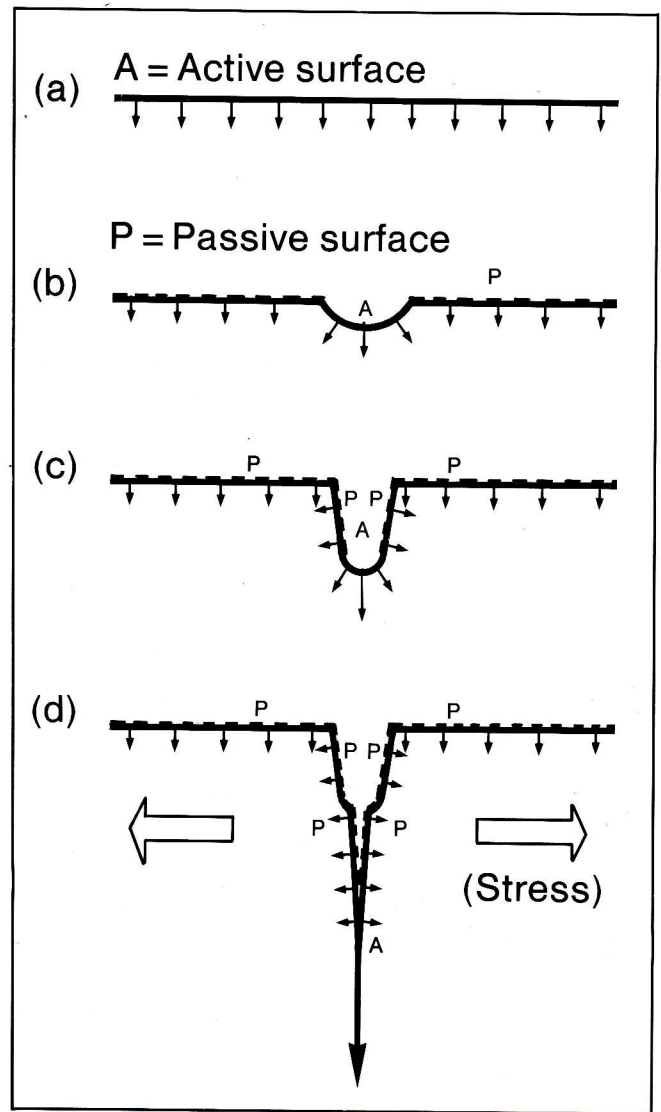
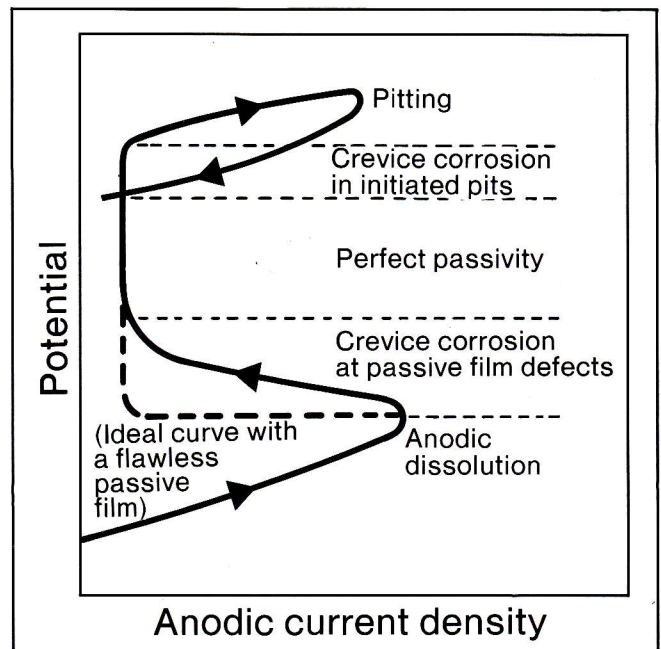


Fig. 7 - Schematic illustration of dissolution rates and distribution in different forms of corrosion. (a) Uniform corrosion; (b) Pitting; (c) Penetrating pitting; (d) Stress-corrosion cracking.

Fig. 8 - Schematic anodic polarization curve for an active-passive system, showing potential ranges for stress-corrosion cracking.



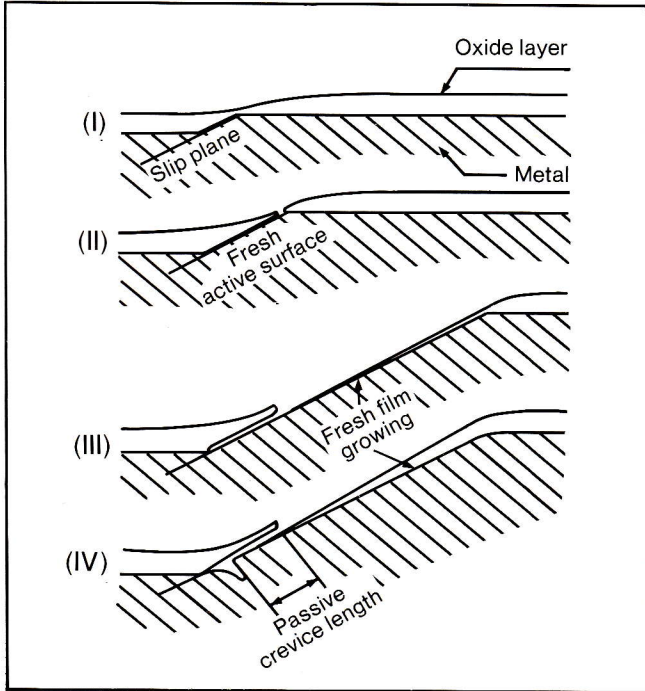


Fig. 9 - Schematic representation of the formation of a micronotch from underfilm crevice attack.

- I. Emergence of a slip step with a necking effect on the oxide film.
- II. Rupture of the oxide film at the leading edge and crevice activation.
- III. Partial passivation of the crevice area and notching penetration at the active foot of the slip step.

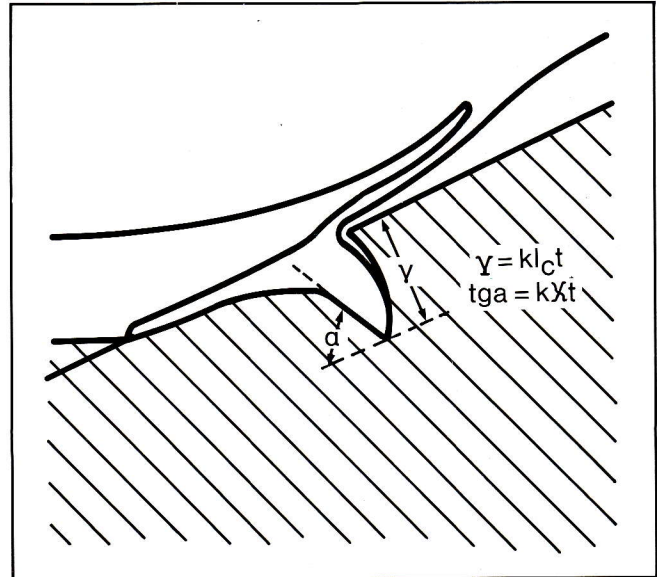


Fig. 10 - Exaggerated initial profile of the micronotch in the active crevice.

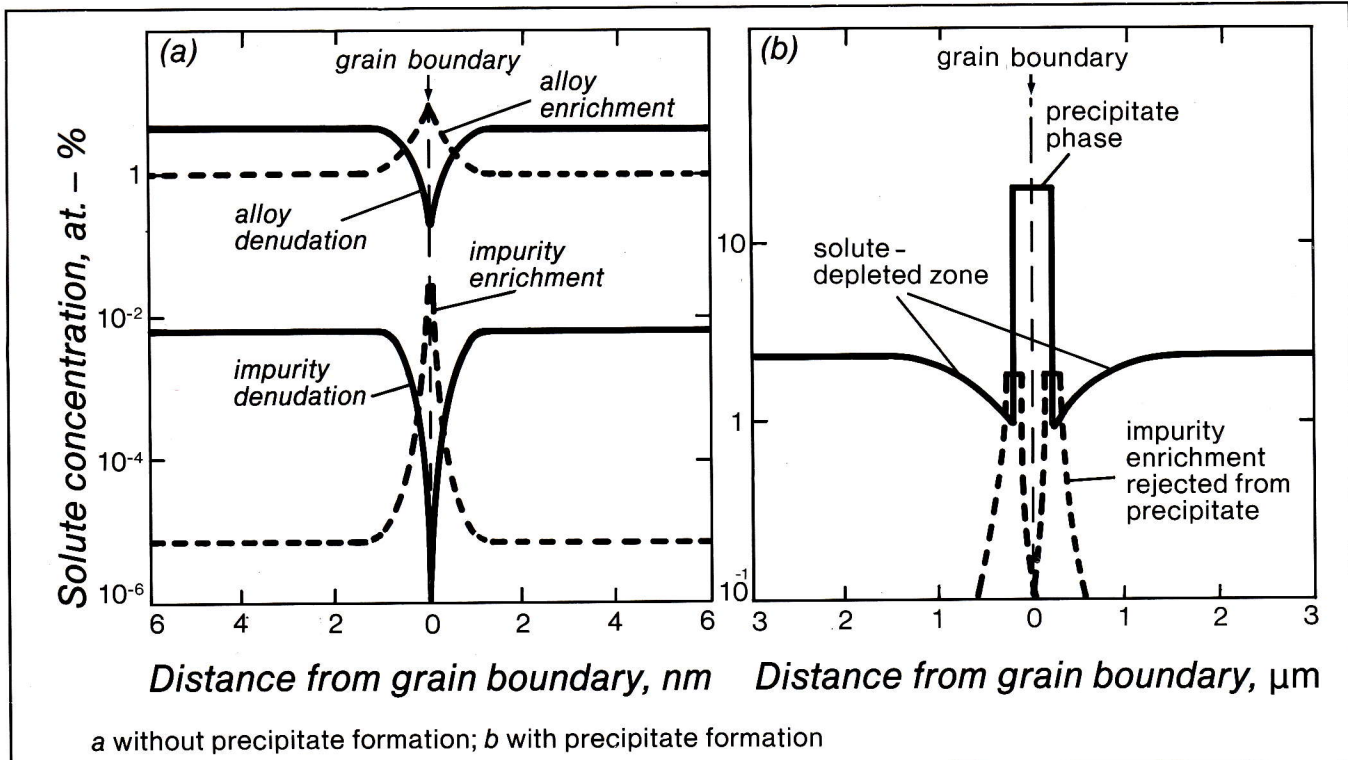


Fig. 11 - Solute concentration profiles at grain boundaries⁽⁴⁾.

A second zone of susceptibility is the high-potential transition range, where, typically in the presence of halide ions, the passivating film undergoes local breakdowns with consequent formation of pits at which passivity cannot be restored unless the potential is reduced below a certain threshold value. Within this instability range, the role of stress would lie essentially in the exploitation of penetrating pitting geometries as critical notches for crack nucleation.

Always, within these transitional ranges, types of localized corrosion somewhat more deleterious than the above non-structurally dependent forms are the structurally dependent attacks pre-eminently represented by selective dissolution at grain-boundary regions, i.e. intergranular corrosion. Grain-boundary regions are usually sites of chemical heterogeneity from segregation of elements in solution in the metal matrix or from preferential concentration of precipitated phases, as schematically illustrated in Fig. 11, according to Staehle.⁽⁴⁾

Because of such localized differentiation in elemental contents affecting the active-passive behaviour, there are several specific media inducing selective

Fig. 12 - Polarization curve of an unsegregated Type 304 stainless steel surface in 1N H₂SO₄⁽⁵⁾.

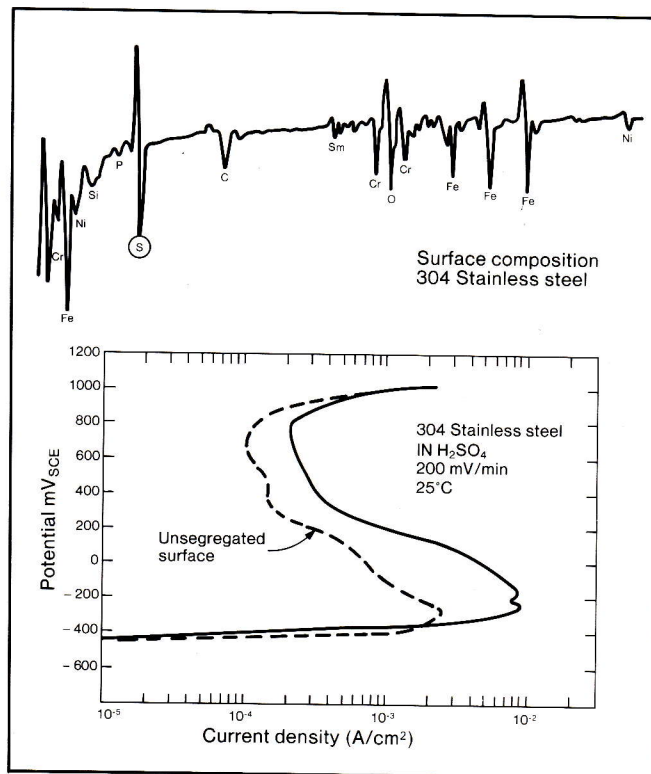
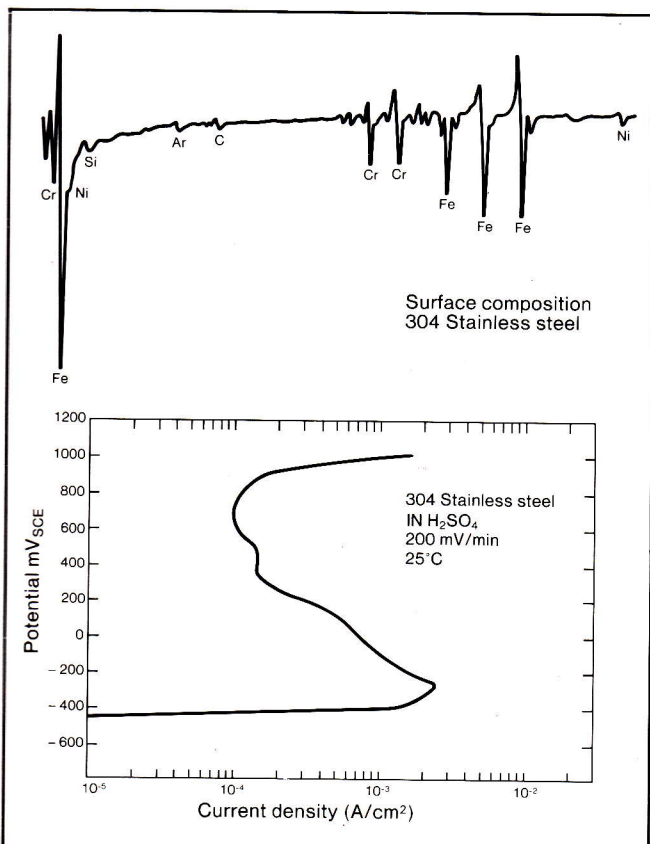


Fig. 13 - Polarization curve of a moderately S segregated surface of Type 304 stainless steel in 1N H₂SO₄⁽⁵⁾.

dissolution in these regions. Well-known examples are nitrate and carbonate solutions with regard to carbon steels and the variety of more-or-less oxidizing media inducing intergranular attack in sensitized stainless steels.

Apart from these most specific cases, there is a recognized relationship between impurity segregation and active-passive electrochemical behaviour. In this connection, Figs. 12 to 16 show anodic polarization curves of AISI Type 304 steel in dilute sulphuric acid for different segregation states obtained by heat-treating under vacuum.⁽⁵⁾ Selective segregation of sulphur (Figs. 13 and 14) appears to increase considerably both critical and passivity current densities, while that of phosphorus (Fig. 16) leads to a smaller increase of the critical c.d. and a decrease in the passivity c.d. Lower effects result from segregating both sulphur and phosphorus (Fig. 15).

In several systems displaying a definite susceptibility to intergranular corrosion, the initial penetration rate on the unstressed material reduces quickly to zero because of the general passivation. In the presence of stress, however, the penetration is sustained and gives rise to intergranular cracks whose growth rate is about

Fig. 14 - Polarization curve of a highly S segregated surface of Type 304 stainless steel in 1N H₂SO₄⁽⁵⁾.

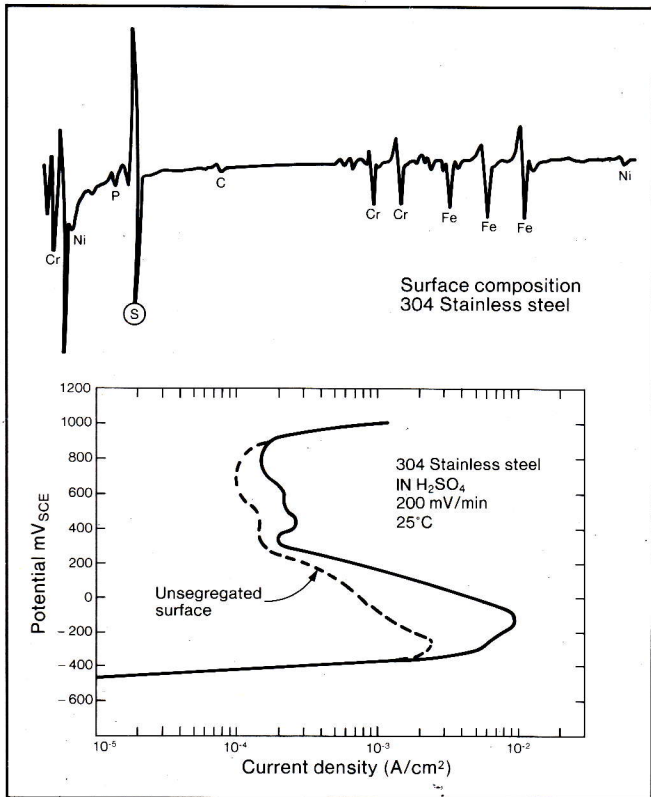


Fig. 15 - Polarization curve of a Type 304 stainless steel surface in 1N H₂SO₄. Both P and S are surface segregants⁽⁵⁾.

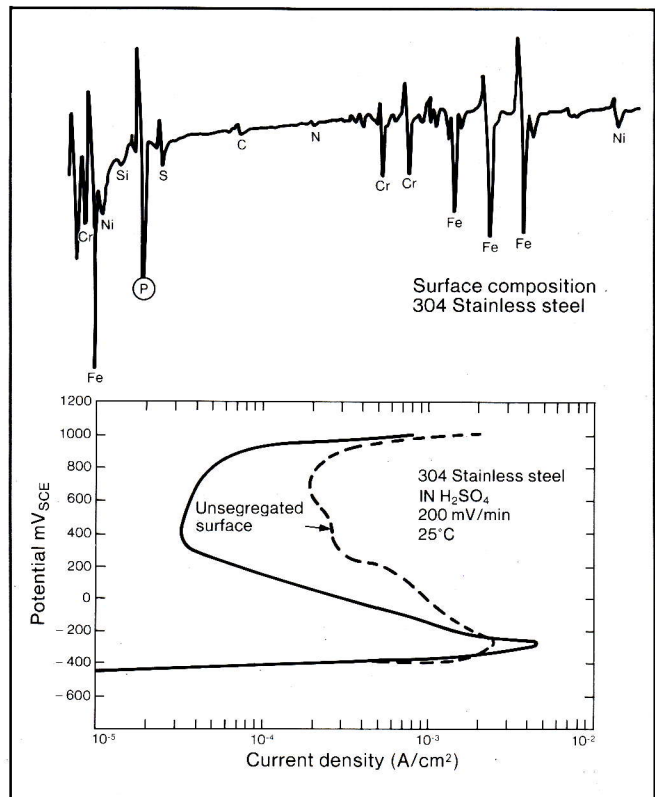
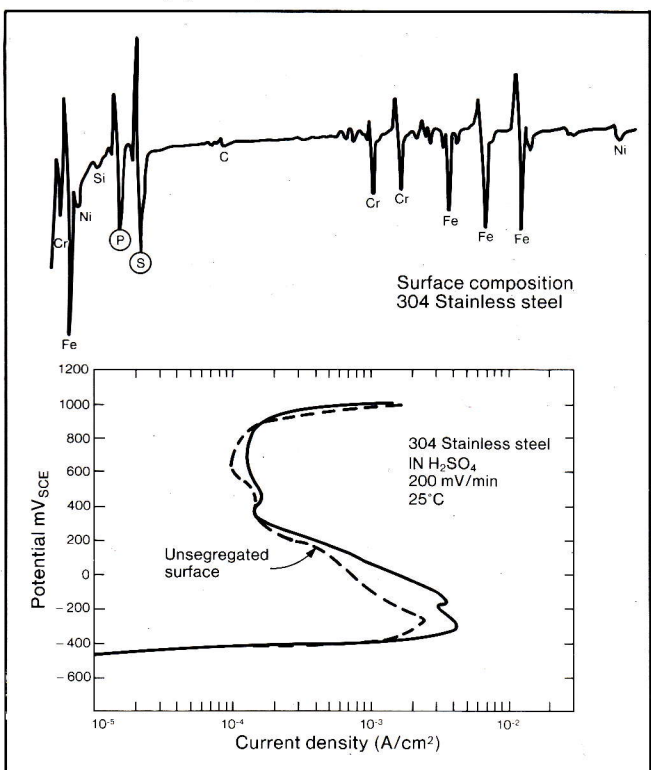


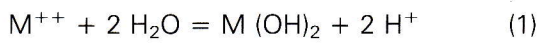
Fig. 16 - Polarization curve of a P segregated surface of Type 304 stainless steel in 1N H₂SO₄⁽⁵⁾.

the same as for the initial attack in the unstressed condition. This means that stress prevents protective filming of grain-boundary regions at the crack tip, so that the subsequent crack propagation is controlled by the dissolution rate in such regions.⁽⁶⁾

Chemistry and electrochemistry within cracks

The chemical composition of solutions enclosed in pits, crevices and cracks has been the object of many theoretical and experimental investigations. Yet, this remains one of the quantitatively most complex and least known aspects in stress-corrosion cracking.

Of course, anodic dissolution at the base of a pit or at the tip of a crack results in hydrolytic acidity from reactions of the type

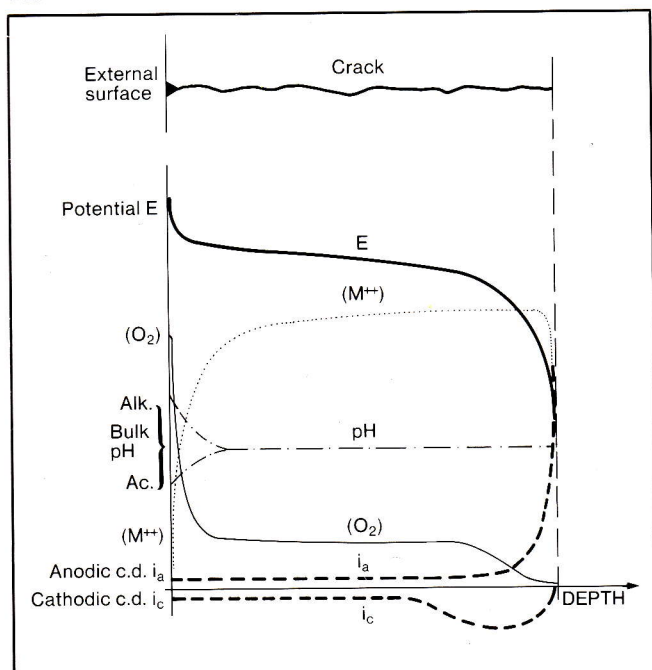


The subsequent neutralization of this local acidity by hydroxyl ions from corresponding cathodic reduction of

oxygen or other oxidizing species would depend on where the cathodic reduction species takes place. While in the initiation stage the cathodic site should be only the external metal surface to which any oxidant had ready access, within a wellgrown crack the relevant electrochemistry, owing to diffusion and resistance polarization, should be rather disconnected from the external surface and the cathodic sites supporting the internal corrosion process should essentially be limited to the crack sides.

As a consequence, the chemical/electrochemical situation within a crack can be envisaged only qualitatively, as roughly schematised in Fig. 17. As for acidity, the enclosed solution should be strongly buffered by cation hydrolysis equilibria according to reaction (1), irrespective of the pH of the external free solution. This would lead to internal pH values around 4 for ferrous alloys.⁽⁶⁾ Concentrations of oxygen or other oxidants may be up to 50 times lower at the crack tip than in the bulk solution.⁽⁷⁾ Concentrations of metal cations should be around molarity i.e. very high with respect to the bulk solutions. Potentials along the crack should be only slightly lower than outside the crack, owing to the passive state at the crack sides and the relatively small ohmic drops,⁽⁸⁻⁹⁾ while the crack tip obviously should be at the free active corrosion potential.⁽¹⁰⁾

Fig. 17 - Schematic illustration of chemical and electrochemical changes within a crack.



Mechanisms of subcritical crack growth

As has been shown, the initiation of stress-corrosion cracking is determined by a critically localized potential-related uncertainty between active and passive behaviour, with the role of stress essentially limited to the production of defects or ruptures in the passivating film.

However, once a crack has nucleated, the question is why and how it undergoes subcritical propagation. In this connection, there is no doubt that the material at the crack tip is in an active state, in front of the relative passivity at the crack sides, with consequent subjection to high-rate anodic dissolution. Under such conditions, there are two possible mechanisms of sharply oriented extension of the nucleated crack. One, as aptly outlined by Parkins,⁽¹¹⁾ results from the existence of highly active paths at the crack tip, while the other is associated with the embrittling decohesive effects of cathodic hydrogen absorbed from the enclosed environment and diffusing to the critically stressed zone ahead of the crack tip. The active path or preferential dissolution mode is typical of low- and medium-strength ductile materials, while high- and ultra-high-strength alloys are most susceptible to hydrogen-induced crack growth.

Active paths may be: (i) pre-existing, i.e. not stress-related, as is the typical case for intergranular stress corrosion cracking in which stress would simply prevent the active grain-boundary regions at the crack tip from being passivated, or (ii) strain-generated, as is generally the case for transgranular stress-corrosion cracking in which the high stress intensity at the crack tip would result in local plastic strain, with consequent generation of a fresh and most active metal surface. In both cases the rate of subcritical crack growth, v_{SCC} , would be Faradaically proportional to the anodic c.d. at the active tip, according to the equation⁽¹²⁾

$$v_{SCC} = i_a M/af\rho \quad (2)$$

where M = atomic weight of the metal, z = valency, ρ = density, F = Faraday's constant, and i_a = anodic c.d. at the active tip, as determined, for instance, by high-rate polarization sweeps allowing the metal surface to remain relatively bare throughout the measurements. Equation (2) expresses plainly that crack growth kinetics in the active path mode is dissolution-controlled. This has been widely confirmed for various ferritic steels in a number of solutions.⁽¹²⁾

As for crack extension induced by hydrogen, a schematic representation of the mechanistic sequence is shown in Fig. 18. Apart from any merely embrittling

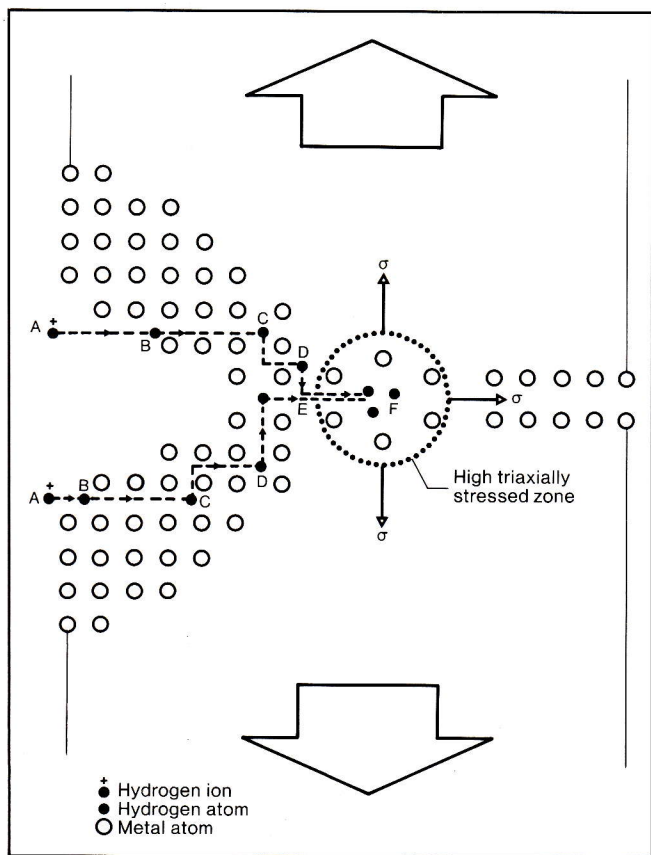


Fig. 18 - Schematic illustration of hydrogen-induced crack extension.
 A-B: H^+ discharge to chemisorbed H atom
 B-C: Solution
 C-D: Lattice diffusion
 D-E: Stress-driven diffusion to the high triaxially stressed zone ahead of the crack tip
 E-F: Critical hydrogen concentration and subsurface crack nucleation.

effect, the key point is the diffusion of dissolved hydrogen to the highly triaxially stressed region ahead of the crack tip, where hydrogen solubility is greatly increased by lattice dilatation. Hydrogen concentration in this zone above certain critical levels would lead, by proton interaction with the 3d electron shell,⁽¹³⁾ to a drastic reduction in cohesive strength, with consequent nucleation of a sub-surface crack and primary crack extension.⁽¹⁴⁾

Surface energy and crack propagation

In relation to the outlined mechanisms of initiation and subcritical growth of stress-corrosion cracks, there is no doubt about the multiple involvement of initially external and subsequently internal surfaces through the following features:

- electrochemical behaviour, as for both thermodynamics (i.e. local potential and e.m.f.s.) and kinetics (i.e. overpotentials and amperometry/coulombometry of equilibration transients, such as from active dissolution, passivation, localized breakdowns in the passivating coverage and subsequent passivity recovery);
 - adhesion (to the substrate), compactness, defectiveness and mechanical properties of the passivating film;
 - elemental segregations and relevant effects.
- It is of the utmost interest, however, to consider the metal surface as a definite metal-environment interface, characterized by a surface energy (i.e. surface tension) with a peculiar role to play in crack propagation.

The adsorption of active species at stressed sites in metal surfaces has been variously considered and criticized as to its influence on the strength of interatomic bonds at the crack tip and, consequently, on the tensile stress for crack extension. Yet, apart from merely influential roles, surface energy has never drawn substantial attention as a primary factor. The Petch-Stables model for hydrogen-induced cracking,⁽¹⁵⁾ linking the susceptibility to a reduction in surface energy due to hydrogen adsorption, has been variously objected to, in relation both to theoretical assumptions and calculation and to experimental verification of embrittlement. As for stress corrosion cracking of low-strength alloys with no susceptibility to hydrogen embrittlement, surface-energy lowering mechanisms have been rejected with similar arguments.

Accordingly, surface energy has so far been regarded only as the specific work required for forming new surfaces in ideally brittle crack extension, pointing out the inferiority, by several orders of magnitude, of such work to that of plastic deformation ahead of the advancing crack tip in practical systems.

The latter appears to be a drastic underestimation of surface effects, overlooking the fact that the curvature of the stressed surface of a "fluid" metal necessarily implies a hydrostatic stress field ahead. Indeed, just because it is generated by highly plastic flow (and not at all by brittle fracture) the tip of a crack should be regarded as a fluid meniscus of atomic dimensions (Fig. 19) giving rise to a capillary pressure drop or an equivalent hydrostatic tensile stress rise, $\Delta\sigma$, across it, expressed by

$$\Delta\sigma = \gamma_M/r \quad (3)$$

where γ_M = metal surface tension and r = radius of curvature. This means to assign a three-dimensional character to the sphere of action of the surface tension

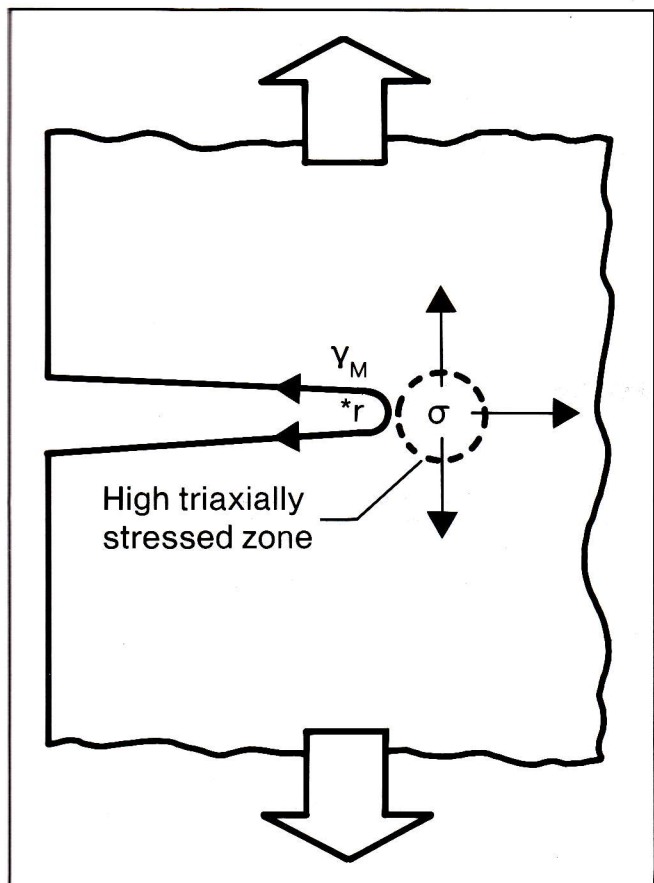


Fig. 19 - Schematic representation of stress equilibrium from capillary forces at a "plastic" advancing crack tip.

on a sharply curved area. Such an "atomic meniscus" would withstand triaxial stresses from applied load up to a critical level $\sigma_c \approx \gamma_M/r$, that is the tensile strength to crack extension.

Ignoring air/metal interactions, γ_M is of the order of 10^{-3} N/mm for common metals and alloys.⁽¹⁶⁾ Thus, with $r = 10^{-6} \div 10^{-7}$ mm, σ_c would be of the order of thousands N/mm², which is much above yield strengths, consistently with the very high stress levels calculated at sharp crack tips.⁽¹⁷⁾

When a liquid is admitted into a crack, interaction with the metal surface leads to the formation of an interfacial surface with a lower energy than in air, i.e. a tension $\gamma_{ML} < \gamma_M$. In consequence, the tensile strength to crack extension would be lower than in air, to an extent depending on the type of electrochemical interaction with the medium.

Ideally polarizable electrodes, e.g. inert metals, are metal/electrolyte interfaces behaving like pure

capacitances. On such electrodes any e.m.f. from electrochemical lack of balance would result in charging up the double layer with no transfer of surface metal atoms, so that γ_{ML} should be always positive and only moderately affected by potential.

On non-ideally polarizable electrodes, on the other hand, any e.m.f. would produce a Faradaic process involving surface atoms, and consequently affecting γ_{ML} . In principle, γ_{ML} could even be negative during anodic dissolution transients, zero when the metal is in thermodynamic equilibrium with its ions in solution, and positive only when (i) the working potential is below the equilibrium potential, as is the case for noble metals or cathodically protected metals, or (ii) the metal is passive, i.e. an interfacial oxide is formed impeding the release of metal atoms and rendering the surface highly or quasi-ideally polarizable in the anodic direction. According to this "energy" hypothesis, the critical situation in stress-corrosion cracking could easily be explained. Indeed, in front of the passivity at all the other exposed surfaces, the active state at the crack tip would lead to anodic dissolution transients (with $\gamma_{ML} < 0$) at any strain- or stress-generated fresh surface with subsequent quick equilibration of the active metal with its ions in solution ($\gamma_{ML} = 0$). Therefore, the crack would be continuously propagable as long as, at its tip, the rate of passivation (i.e. recovery of a positive surface tension) is definitely lower than the rate of activation (i.e. active surface formation) from plastic straining or passive film rupturing.

The substantiation of this propagation model, assigning a driving role to surface energy, however, requires much basic research on the actual relationship between working potential and surface tension in active-passive systems of practical interest.

Evaluation of susceptibility

Experimental methods of use result directly from the above mechanisms and relevant influential factors. Consistently with the essence of the processes involved in initiation and first growth stages, most techniques are basically electrochemical.

Apart from stress, a prerequisite for susceptibility is that the metal-environment system displays an active-passive behaviour. This can be drawn by ordinary potentiodynamic anodic polarization curves at constant scanning rates. Active-passive or passive-active transitions may be rather inherent properties of materials, as is usually the case for the passivation of stainless steels, superalloys and titanium-and aluminium-base alloys, or, instead, properties induced by specific species present in the exposure medium, as

is the case for the relative passivation of carbon and low-alloy steels in nitrate, carbonate and caustic solutions as well as for localized passivity breakdown induced by halide ions on inherently passive alloys.

Polarization curves also show the electrochemical conditions (i.e. working potentials) at which hydrogen production and consequent ingress into the metal can occur. Further, these curves reveal the effects of thermomechanical history on the transitional behaviour of a material, either through final microstructure and metallurgical defectiveness or through surface segregation of critical elements.

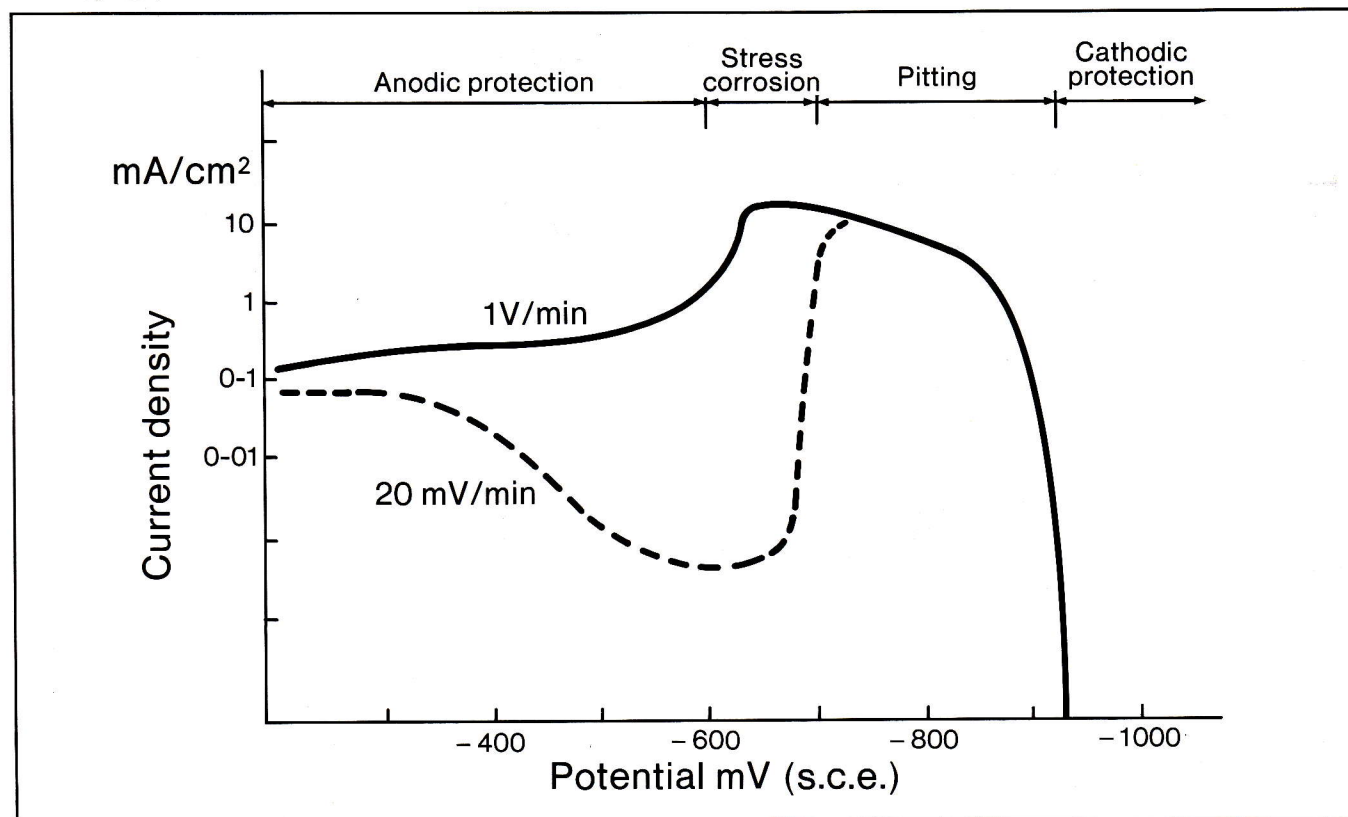
Another electrochemical approach of great relative meaning consists in recording the anodic current decay at various potentials. A transitional condition implies, indeed, that the anodic c.d. on a polarized metal surface reduces substantially with time, and the relevant kinetics of decay on an initially bare surface can give some indication of proneness to stress corrosion cracking. Namely, too low current densities and too high decay rates denote a passivating potency overcoming any possible trend towards crack

nucleation, whereas too high current densities and too low decay rates denote conditions too active for cracking. As has been found in studying a variety of systems, susceptibility must be looked for at intermediate conditions, properly indicative of a critical balance between passivation and activation kinetics.

The electrochemical technique of the utmost use for delineating susceptibility conditions in terms of critical potential ranges is differential sweep-rate anodic polarization.⁽¹⁸⁾ This method consists in comparing a potentiodynamic polarization curve obtained at a relatively high scanning rate (say, thousands mV/min) with a curve obtained at a relatively low sweep rate (say, tens mV/min). The critical potential ranges are those within which differences between high sweep rate current densities (related to a quasi film-free or active metal surface) and low sweep rate current densities (related to a well-filmed or passive surface) are the greatest. A definite example for steel in carbonate-bicarbonate solution is given in Fig. 20,⁽¹²⁾ while Fig. 21⁽¹²⁾ shows the validity of the technique for three most typical systems.

In practice, however, it has been found⁽¹²⁻¹⁹⁾ that only

Fig. 20 - Differential sweep rate polarization curves for C-Mn steel in 1N Na₂CO₃ + 1N NaHCO₃ at 90°C⁽¹²⁾.



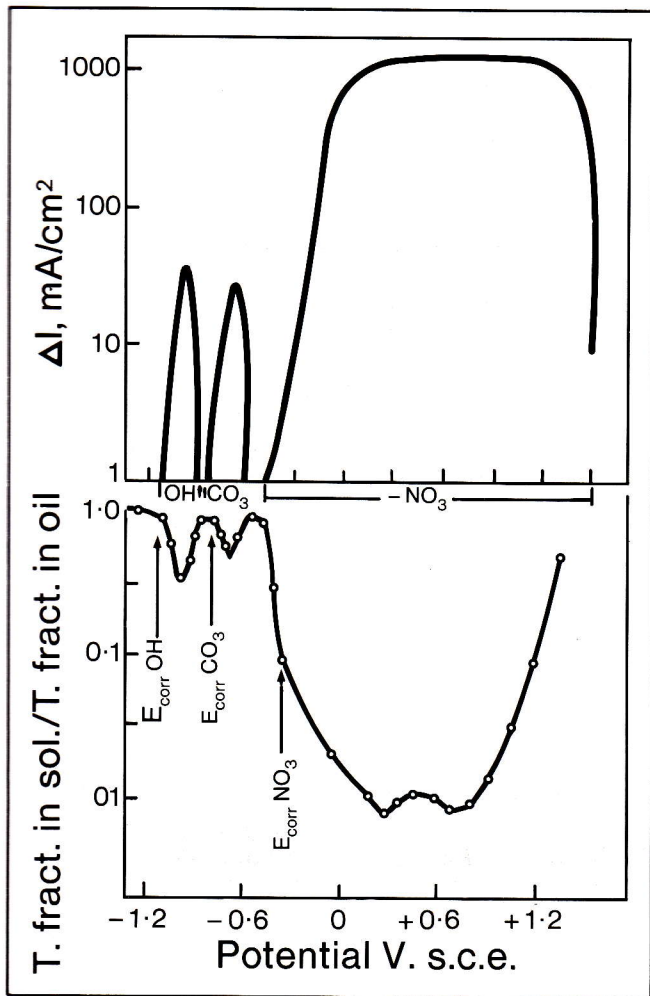


Fig. 21 - C.d. differences between fast and slow sweep rate polarization and stress corrosion cracking susceptibility for steel in NO_3 , OH and $\text{CO}_3\text{-HCO}_3$ environments⁽¹²⁾. (E_{corr} = Free corrosion potential)

fast-rate current densities, higher than 1 mA/cm^2 , and c.d. differences over 1000 times as high as slow-rate current densities, must be regarded as definitely indicative of susceptibility.

Besides basic techniques for studying predisposition and influences, there are specific techniques for the quantitative evaluation of stress-corrosion cracking in susceptible systems. Simple time-to-rupture tests under constant load or constant strain are of use only for short-incubation or high-growth-rate systems, and are rather impracticable for most systems characterized by long, and/or not very reproducible, incubation times under static working conditions. The most complete and significant technique for the latter systems is the constant slow-strain-rate test to rupture. If, indeed, the strain rate is low enough (say, $10^{-5} \div 10^{-7} \text{ s}^{-1}$) to

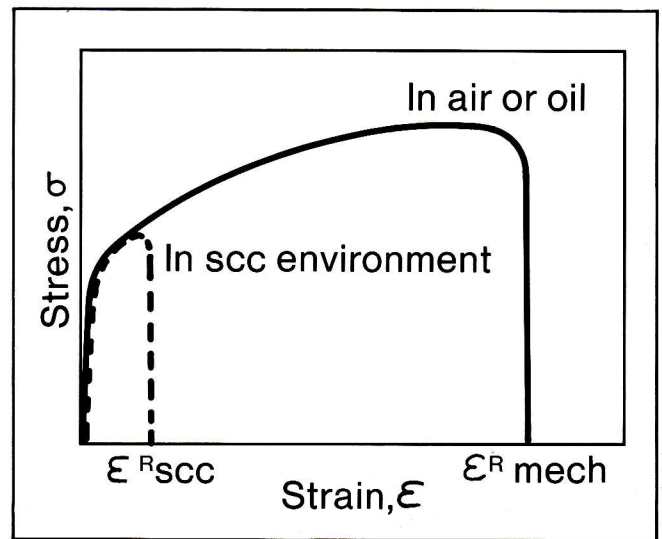
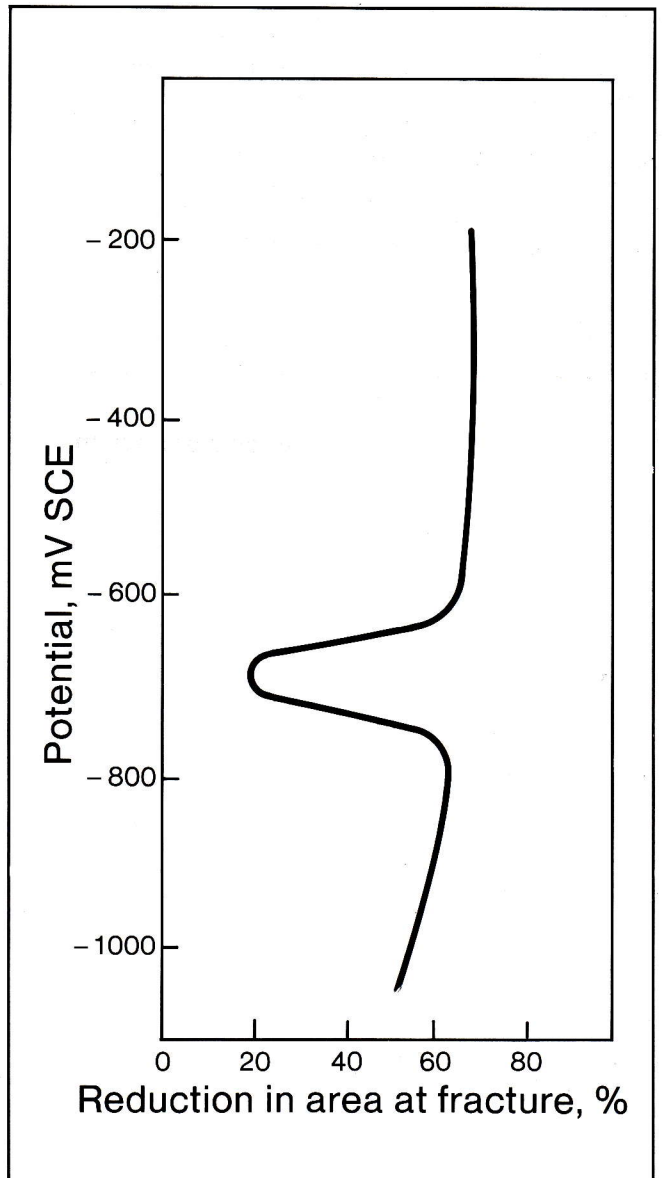


Fig. 22 - Schematic illustration of stress-corrosion cracking effects in terms of reduction of rupture work in constant strain rate test.

Fig. 23 - Reduction in area at fracture vs Potential (from constant strain rate tests) for carbon steel in $1\text{N Na}_2\text{CO}_3 + 1\text{N NaHCO}_3$ at 90°C ⁽¹²⁾



allow the metal-environment interaction time to exert its fissuring power, an impressive demonstration results, consisting in a drastic reduction in the fracture work with respect to the same test carried out in air or oil. As shown in Fig. 22, two quantitative indices are obtained: (i) the relative decrease of reduction in area at fracture and (ii) the relative decrease of tensile stress at rupture. By testing at various (constant) potentials, either index can be plotted against potential, as shown for a typical system in Fig. 23,⁽¹⁸⁾ clearly delineating the range of susceptibility and the extent of the effects.

Such curves, giving fracture behaviour as a function of the electrochemical working conditions, are of great value either as a means of technological research on metallurgical solutions to the problem of stress corrosion, or as a reliable reference for stress-corrosion prevention through chemical or electrochemical control of the environment. Considering, for instance, the curve shown in Fig. 23, it is easily understood that a small addition of a suitable oxidant to the medium or a slight anodic polarization of the exposed steel can succeed in shifting the working potential definitely out of the susceptibility range, so rendering the system

completely safe and monitorable through simple potential measurements.

Potentiality of surface metallurgy for prevention

Since stress-corrosion cracks nucleate at exposed tensile-stressed surfaces, it appears that metallurgical treatments inducing definite chemo-mechanical modifications in the surface layer can provide substantial protection to susceptible alloys.

A most simple and well-known treatment is controlled shot-peening. As illustrated in Fig. 24, uniformly impacting a metal surface with a suitable granular material can produce a high (pre) compressive stress in the surface layer, even if the latter is initially tensile-stressed by an ordinary fabricating procedure. Compressive stresses in the order of the yield strength of the material (i.e. surpassing tensile stresses from subsequent loading) can be obtained up to several ten μm depths. A few impressive experimental results for a most typical system are pointed out in Table 1.

TABLE 1 - Effect of shot-peening on stress-corrosion cracking of U-bent specimens of type 304 stainless steel in boiling 42% MgCl_2 ⁽²⁰⁾

Heat treatment	Surface treatment	Time-to-failure
16 h at 540 °C	None	3 h
16 h at 540 °C	Shot-peening	No f. in 103 h
144 h at 565 °C	None	10 h
144 h at 565 °C	Shot-peening	No f. in 202 h

Other methods of great potential use are those based on laser metallurgy by which an ultra-high-rate thermal cycle, consisting of heating up to melting and subsequent cooling down to ordinary temperatures, is imposed on the metal surface, so that a near-amorphous layer of metastable phase can be obtained with drastic elimination or minimization of selectively dissoluble grain-boundary regions. Micrographs in Fig. 25⁽²¹⁾ give an impressive picture of such effects for a carbon-steel on which a surface layer of non-crystalline martensite is formed over the normal ferrite-pearlite microstructure.

Finally, besides the well-known chances of electroplating and diffusion coating, special

consideration must be given to the technique of ion implantation by which "non-thermodynamic" surface alloying can be obtained. Fig. 26 shows the effects of surface implantation with aluminium and titanium ions on the electrochemical response of 316 L stainless steel. The potential range of non-recoverable passivity from electrochemical pitting appears to be strongly restricted on implanted surfaces with inferable implications on transitional behaviour and stress-corrosion cracking susceptibility.

Remarks in conclusion

- Stress-corrosion cracking is an "all-surface" process

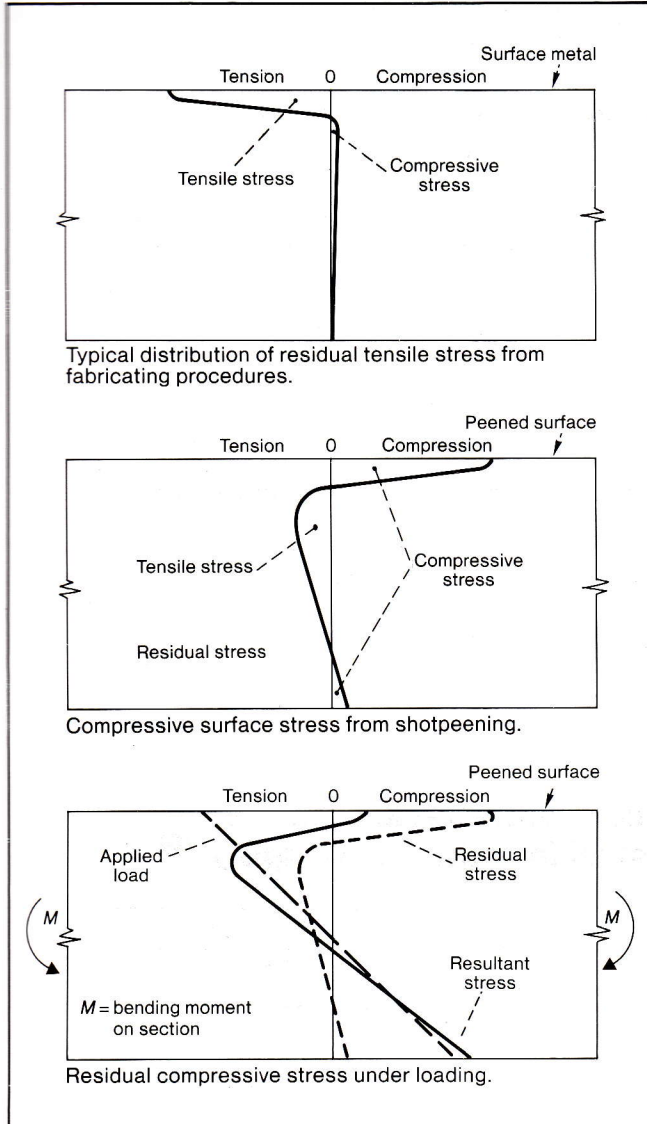


Fig. 24 - Schematic illustration of the effect of shot-peening on surface stresses in a metal beam^[20].

occurring in active-passive systems under transitional conditions. At first, through stress-induced or stress-favoured localized defects or break-downs in the passivating film, and, soon after, through stress-sustained surface activation at the crack tip, it succeeds in baffling great resistive energies of metallic volumes leading to drastically brittle fissuring even in most ductile and tough alloys.

● Reliable means of prediction and control of environmental stress cracking can result only from theoretical and experimental knowledge of metal surfaces in relation to:

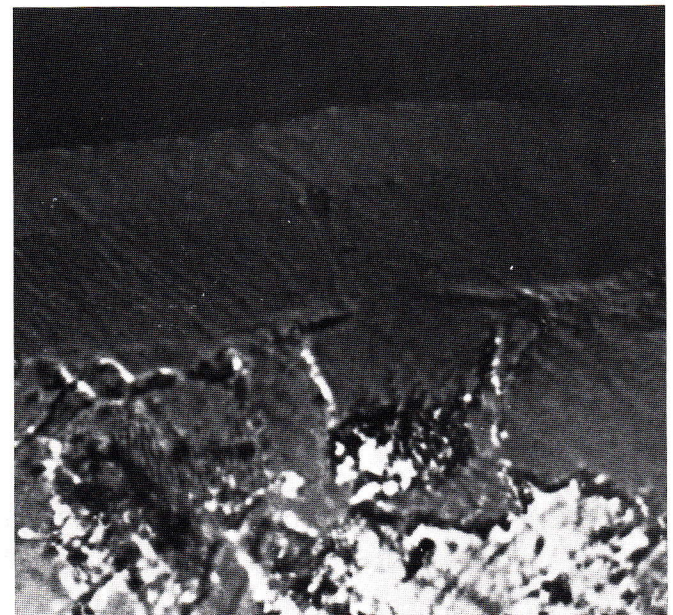
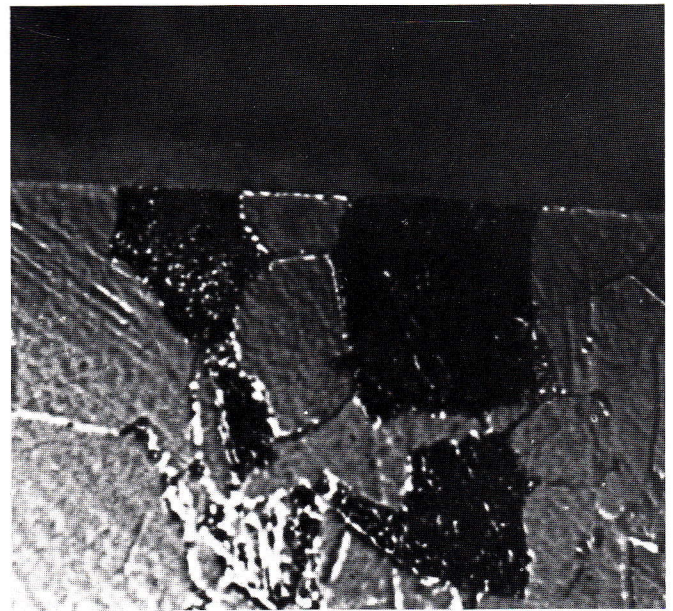


Fig. 25 - Effect of laser surface melting/rapid quenching on the surface of a 1040 steel^[21].

- Analytical features, as for selective segregations and precipitations;
 - Microstructural features, as for emergence of lattice defects and slip planes;
 - Electrode behaviour, either in the active state implying a Faradaic i.e. metal-consuming interaction with the environment or in the passive state conferring high anodic polarizability;
 - Oxide films, as for composition, structure, thickness, defectiveness and mechanical properties, as well as adhesion and defects of adhesion to the metal substrate;
 - Chemistry of "inter-surface" solution enclosed within cracks;
 - Surface energies at critical metal-environment interfaces such as crack tips.
- Potent means for controlling stress-corrosion cracking appear to be attainable by surface-metallurgy treatments, provided that low-cost and practicable application techniques can be developed.

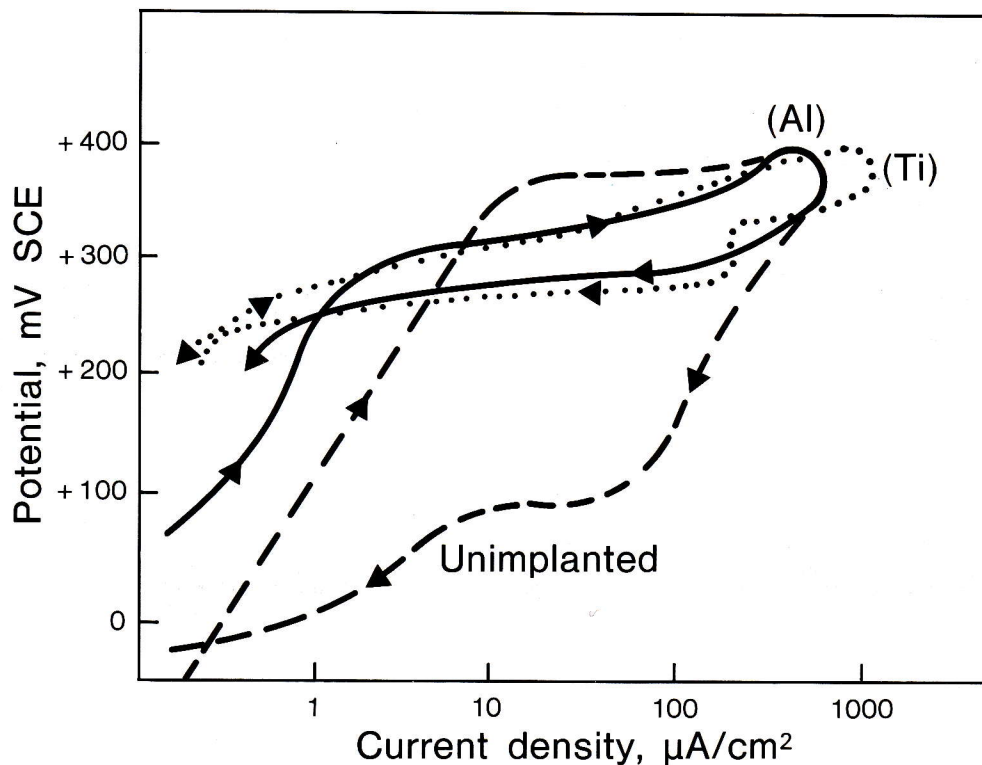


Fig. 26 - Effects of ion implantation with aluminum and titanium on cyclic anodic polarization response of Type 316L stainless steel in air-saturated 3.5% NaCl solution⁽²²⁾.

REFERENCES

- (1) Sandoz, G. A unified theory for some effects of hydrogen source, alloying elements, and potential on crack growth in martensitic AISI 4340 steel. *Metall. Trans.*, **3** (1972), 1169-1176.
- (2) France, Jr., W. D. Crevice corrosion of metals. Review paper presented at *Symposium on Localized Corrosion, ASTM Annual Meeting*, Atlantic City, June 29, 1971, pp. 1-47.
- (3) Bombara, G. The role of oxide films in stress corrosion cracking initiation. *Corros. Sci.*, **19** (1979), 991-999.
- (4) Staehle, R. W. Environmentally enhanced cracking of engineering alloys. In K. J. Miller and R. F. Smith (Eds.), *Mechanical behavior of materials*. Pergamon Press, Oxford, 1980, vol. 1, pp. 93-108.
- (5) Chaung, H., and J. B. Lumsden. Electrochemical response of surface segregated 304 stainless steel. In *Corrosion and corrosion cracking of materials for water cooled reactors*. EPRI Progress Report, Fontana Corros. Center, Columbus, Oh., 1977, p. 43-49.
- (6) Parkins R. N. Electrochemical influences in fracture initiation. *Metals Technology*, **9** (March-Apr. 1982), 122-129.
- (7) Turnbull, A. Theoretical evaluation of the dissolved oxygen concentration in a crevice or crack in a metal in aqueous solution. *Br. Corros. J.*, **15** (1980), 162-171.
- (8) Melville, P. H. Variation of potential in stress corrosion cracks. *Br. Corros. J.*, **14** (1979), 15-19.
- (9) Ateya, B. G., and H. W. Pickering. Electrochemical processes within cavities and their relation to pitting and cracking. *J. Electrochem. Soc.*, **122** (1975), 1018-1026.
- (10) Doig, P., and P. E. J. Flewitt. Limitations of potentiostatic control in stress corrosion crack growth measurements. *Metall. Trans.*, **9A** (1978), 357-362.
- (11) Parkins, R. N. Stress corrosion cracking of low-strength ferritic

steels. In J. C. Scully (Ed.), *The theory of stress corrosion cracking in alloys*. Nato, Sci. Affairs Div., Brussels, 1971, pp. 167-185.

- (12) Parkins, R. N. Predictive approaches to stress corrosion cracking failure. *Corros. Sci.*, **20** (1980), 147-166.
- (13) Barth, C. F., and E. A. Steigerwald. Discussion of evaluation of hydrogen embrittlement mechanisms. *Metall. Trans.*, **2** (1971), 1988-1989.
- (14) Johnson, H. H., J. G. Morlet, and A. R. Troiano. Hydrogen crack initiation and delayed failure in steel. *Trans. AIME*, **212** (1958), 528-536.
- (15) Petch, N. J., and P. Stables. Hydrogen adsorption and surface energy. *Nature*, **169** (1952), 842-850.
- (16) Heady, R. B. The Petch-stables theory of hydrogen embrittlement. *Corrosion*, **33** (1977), 442-447.
- (17) Rice, J. R. Some mechanics research topics related to the hydrogen embrittlement of metals. *Corrosion*, **32** (1976), 22-26.
- (18) Sutcliffe, J. M., R. R. Fessler, W. K. Boyd, and R. N. Parkins. Stress corrosion cracking of carbon steel in carbonate solutions. *Corrosion*, **28** (1972), 313-320.
- (19) Holroid, N. J. H. *Prediction of susceptibility to stress corrosion cracking*. Ph. D. Thesis, University of Newcastle upon Tyne, 1977.
- (20) Daly, J. J. Controlled Shotpeening prevents stress corrosion cracking. *Chem. Engn.*, Feb. **16** (1976), 113-116.
- (21) Draper, C. W., and C. M. Preece. Courtesy micrographs. *Mat. Perform.*, **19** (Nov. 1980), cover.
- (22) Bombara, G., M. Cavallini, G. Dearnaley, P. D. Goode, and R. Fratesi. The effect of ion implantation on the resistance of 316L stainless steel to crevice corrosion. *Surface Techn.*, **18** (1983), 21-30.