

# ENHANCED STRESS CORROSION RESISTANCE FROM STEELS HAVING A DUAL-PHASE AUSTENITE-MARTENSITE MICRO-STRUCTURE

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## ABSTRACT

A high strength steel with an austenite-martensite duplex microstructure has been produced by extruding nickel-coated steel powder. The austenite is stable and is present as a continuous network surrounding a high strength martensite. The dual-phase steel exhibits superior resistance to stress corrosion cracking in 3.5% NaCl solution compared with steels of similar strength having conventional microstructures.

KEYWORDS steel; stress corrosion;  $K_{TH}$ ; dual-phase; austenite; martensite.

## INTRODUCTION

The major limitation to the use of high-strength steels in engineering applications has been their high susceptibility to stress corrosion cracking. Although several attempts to improve air fracture toughness  $K_{IC}$ , have been successful, these have not usually resulted in corresponding improvements in the threshold stress intensity factor  $K_{TH}$ . The basic problem is that the martensite microstructure that is essential for high strength is inherently susceptible to embrittlement by hydrogen which arises from the corrosive action of the environment. One of the potential solutions to this problem is to develop steels having dual-phase microstructures in which separate constituents are responsible for the conflicting property requirements. A tempered martensite phase must remain as the source of strength. The obvious choice of constituent for conferring resistance to fracture is austenite. Being a low strength material with high work hardening capacity, austenite is inherently tough. More importantly, hydrogen has a high solubility in austenite but does not give rise to significant embrittlement. Consequently an appropriate dispersion of austenite has the potential to act as both a mechanical crack arrestor and a trap for hydrogen.

If austenite is to be effective in a dual-phase microstructure, it must be stable. Also if it is to act as an efficient barrier to the transport of hydrogen, it should ideally be present as a continuous phase surrounding the martensite. Venkatasubramanian and Baker (1980) have shown that such a microstructure can be achieved by coating high strength steel powder with a layer of nickel followed by hot extrusion to produce a fully dense product.

### EXPERIMENTAL

The present investigation is concerned with steels having yield strengths in the range of 1300 MPa to 1750 MPa. To achieve these strength levels a medium carbon chromium-vanadium steel was selected conforming to AISI 6150.

In order to obtain uniformity of size and shape and to avoid the problem of the high oxygen content of air-atomized powder, it was decided to produce clean 'powder' of constant size and shape by chopping bright drawn wire into short lengths. Two batches of wire having diameters of 0.6 mm and 0.2 mm were obtained, each batch being chopped automatically into 1 mm lengths. The chopped wire particles were chemically cleaned and then electroplated with nickel. For each wire size, the coating thickness was adjusted so as to obtain a nickel volume fraction of nominally 5%. After washing and drying, the plated particles were packed into mild steel cans, evacuated and sealed. The cans were heated for 3 hours at a temperature of 1000°C and extruded to give 25 mm by 12.5 mm rectangular section bar. For comparison with the plated material, similar extrusions were produced from unplated wire. Also, in order to determine whether the use of wire as a starting material would have any effect on properties, a conventional steel ingot of similar composition to that of the wire was cast and extruded to produce the same section as the wire material.

The extrusion ratio of 14 resulted in complete consolidation of the powder, the unplated material being indistinguishable from the extruded cast steel. The microstructure of the plated wire material is illustrated in Fig. 1(a) and 1(b). The transverse section shows that the nickel has diffused into the steel giving rise to a dual-phase microstructure consisting of a continuous uniform layer of austenite surrounding a medium-carbon martensite. The longitudinal section shows that during the extrusion the wire particles have been drawn out to produce fibres of martensite, each of which is completely surrounded by austenite.

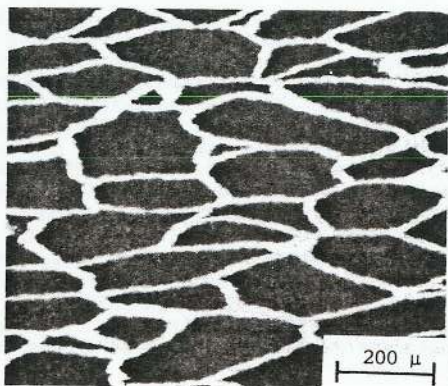


Fig. 1a Dual-phase steel transverse section.

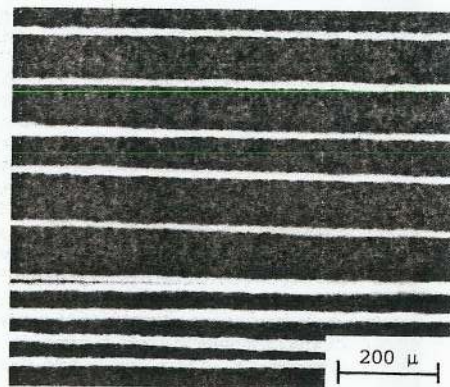


Fig. 1b Dual-phase steel, longitudinal section.

Heat treatment of all the extruded material involved austenitisation at 870°C followed by oil quenching. Because of the effect of nickel in depressing the martensite start temperature, the quenched specimens were cooled to -196°C in order to ensure the transformation of any metastable austenite. Tempering was carried out at temperatures in the range 150°C to 490°C to produce yield strengths between 1300 MPa and 1750 MPa.

To determine the stress corrosion cracking behaviour, 10mm by 20mm section, single-edge notched bend specimens were tested in an environment of 3½% NaCl solution. The pre-cracked specimens were tested under conditions of constant mouth-opening displacement, the rate of crack growth being determined continuously as a function of stress intensity. The tests were terminated when the crack growth rate had fallen to less than 10<sup>-6</sup>mm/sec. The test piece was then broken open in air, thus permitting an accurate determination of the final crack length. The corresponding stress intensity factor was taken as the threshold value.

### RESULTS

For all the strength conditions tested, the stress corrosion crack growth behaviour exhibited similar characteristics. Initially the growth rate tended to be independent of the stress intensity, i.e. conventional stage II behaviour. As the stress intensity decreased, a transition occurred to stage I behaviour where the growth rate rapidly decreased towards a threshold stress intensity value,  $K_{TH}$ . An interesting difference between the conventional and dual-phase microstructures was that in the case of the former, the load decreased smoothly to the threshold state whereas in the dual-phase material, the load decreased in a series of discontinuous steps. The latter implies that crack growth is discontinuous in the dual-phase structures.

In Fig. 2,  $K_{TH}$  is plotted against yield strength and it is immediately apparent that the dual-phase structures have superior stress corrosion performance. The improvement in  $K_{TH}$  increases with increasing strength and at a yield strength of 1750 MPa the dual-phase structure shows a 75% increase in  $K_{TH}$  as compared to the conventional steel. The results from both wire sizes are plotted in Fig. 2 and there would appear to be no significant effect of martensite 'grain' size or boundary layer thickness for a given volume fraction of austenite. As far as the conventional microstructures are concerned, the cast-extruded and wire-extruded materials exhibit similar behaviour.

In Fig. 3 the stage II crack growth rate is plotted against yield strength for all of the conditions tested. At very high strength levels the crack growth rate in the dual-phase steel is considerably less than in the conventional steel. However, the surprising difference between the conventional and dual-phase steels is the variation of crack growth rate with yield strength. Whereas the conventional steel shows the well-recorded behaviour of decreasing growth rate with decreasing strength, in the dual-phase steel the crack growth rate tends to decrease as the strength increases.

In the steel having a conventional tempered martensite structure, the micro-mechanism of stress corrosion cracking was intergranular separation, this being the usual mode of hydrogen-assisted fracture in high strength steels. In the dual-phase structures the tempered martensite fractured in a predominantly intergranular manner whilst the austenite separated by a ductile mechanism (Fig. 4). In all cases the stress corrosion crack terminated at the austenite. This is clearly illustrated in Fig. 5 which provides a sectioned view of an arrested stress corrosion crack. It is important to note that a number of isolated cracks have formed in the martensite phase ahead of the main crack with the surrounding austenite phase remaining intact. This offers an explanation for the observed discontinuous nature of crack advance

in the dual-phase steels and is also clear evidence for hydrogen being the dominant cause of embrittlement in the stress corrosion cracking of steels in salt water.

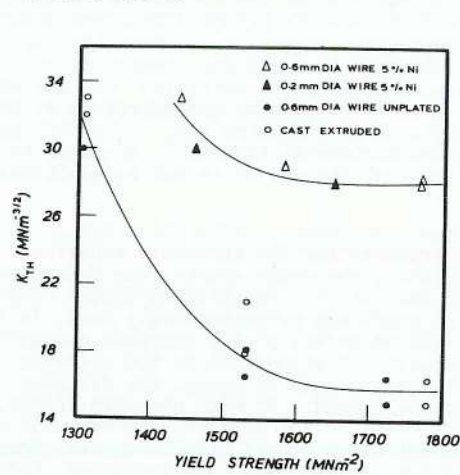


FIG. 2. Yield strength dependence on  $K_{TH}$  for dual-phase and conventional steels

#### DISCUSSION

The present investigation has demonstrated that dual-phase microstructures of austenite and martensite can exhibit very high strength combined with outstanding resistance to stress corrosion cracking. The austenite phase is obviously much softer than the martensite and it has been found that the strength of the "composite" obeys a rule of mixtures relationship. Consequently, in order to achieve comparable strengths between the dual-phase and conventional microstructures, the former has to be tempered at a lower temperature. It follows that when comparing the microstructures at the same nominal strength, the martensite in the dual-phase steel must be harder than that in the conventional steel. Usually an increase in hardness is accompanied by an increased susceptibility to hydrogen-assisted cracking. The fact that the dual-phase steels exhibit enhanced resistance to cracking demonstrates the dominant influence of the austenite phase.

In conventional tempered martensites the most widely-held view of the mechanism of stress corrosion cracking is that it is a stress-controlled brittle fracture phenomenon caused by the presence of dissolved hydrogen in the region of stress concentration ahead of the crack tip. (Support for this mechanism is provided by Fig. 5 which shows isolated micro-cracks ahead of the main crack tip). In order to permit crack advance it has been suggested that a certain critical stress must be achieved over some microstructurally significant distance ahead of the crack tip. The value of the critical fracture stress depends on two main factors; the composition and microstructure of the steel, and the local concentration of dissolved hydrogen. The latter is controlled by the hydrogen activity of the environment, the permeability of the steel, the magnitude of the stress triaxiality

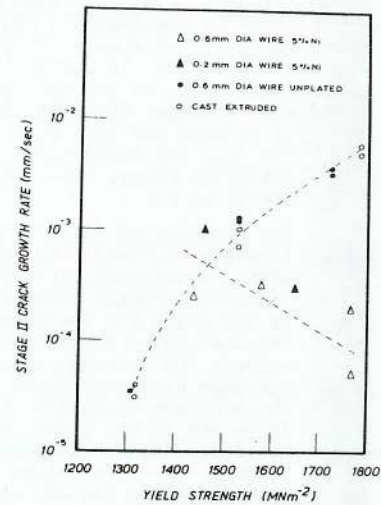


FIG. 3. Yield strength dependence of stage II crack growth rate

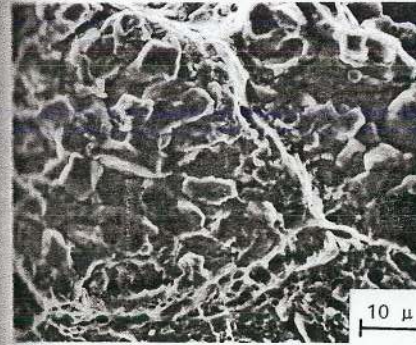


Fig. 4 Dual-phase steel, stress corrosion fracture.

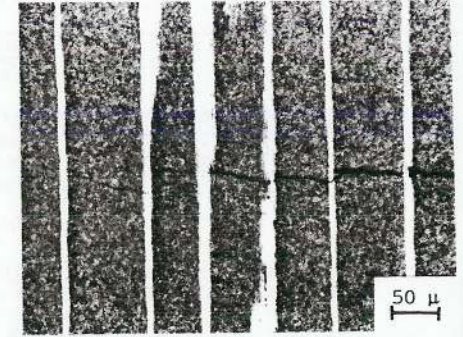


Fig. 5 Dual-phase steel, arrested stress corrosion crack.

ahead of the crack tip and the distance of the fracture initiation site ahead of the crack tip. In the case of the dual-phase microstructures, the presence of the continuous austenite phase can influence the susceptibility to cracking by modifying both the local hydrogen concentration and the stress distribution ahead of the crack tip.

The permeability of hydrogen in austenite is much less than in ferrite. However, the fact that the dual-phase microstructures exhibit hydrogen-assisted crack growth demonstrates that hydrogen transport can occur through the austenite phase, presumably by a dislocation-assisted transport mechanism. At high stress intensities, the region of stress intensification ahead of the crack tip is extensive and the conditions necessary for the nucleation of a micro-crack can be satisfied at low hydrogen concentrations. Under these conditions, microcracks develop in the isolated 'grains' of martensite ahead of the main crack. A consequence of the crack development and the high stress intensity is that there is a relatively large displacement of the crack faces at the original crack tip position. This causes the intervening ligament of austenite to separate by a strain-controlled ductile fracture mechanism. In this way the crack is able to advance, albeit in a discontinuous manner.

As the stress intensity decreases, it becomes progressively more difficult to satisfy both the critical stress requirement for the nucleation of micro-cracks and the local strain requirement necessary to cause rupture of the remaining bridges of austenite. The situation at threshold is most clearly illustrated by reference to Fig. 5. At this stage, microcracks have formed in the martensite ahead of the crack tip but are prevented from joining by the intervening bridges of austenite.

Having considered the nature of crack advance in the dual-phase steel, it is appropriate to examine the mechanisms by which austenite improves the  $K_{TH}$  of the dual-phase microstructure. The unbroken ligaments of austenite which are highly stressed, exert a closing force on the crack flanks. The effect of this closing force on the crack tip stress intensity can be evaluated as follows.

Consider a crack of length 'a' with a point force 'F' acting at a distance 'c' from the crack tip. If  $c \ll a$ , then the stress intensity due to F is

$$K_F = \sqrt{\frac{2}{\pi}} \frac{F}{\sqrt{c}} \quad (\text{Tada et al. 1973})$$

If, instead of the point force, a uniform stress 'p' acts over the distance c, then the stress intensity due to p is given by:

$$K_p = \sqrt{\frac{2}{\pi}} \frac{c}{\sqrt{a}} \frac{pda}{\sqrt{a}} = \frac{2\sqrt{2}}{\sqrt{\pi}} p\sqrt{c} \dots\dots\dots(1)$$

Assuming that all the austenite ligaments have yielded, the closure stress exerted by the unbroken ligaments is  $f\sigma_y$  where f is the volume fraction of austenite and  $\sigma_y$  is the effective flow stress in the austenite. The negative K exerted by the ligaments is then given by

$$K_L = \frac{2\sqrt{2}}{\sqrt{\pi}} f\sigma_y\sqrt{c} \dots\dots\dots(2)$$

For a crack of length a, subjected to a stress intensity K, the crack face displacement u at a distance c from the crack tip is given by:

$$u = \frac{4\sqrt{2}}{\sqrt{\pi E'}} K\sqrt{c} \dots\dots\dots(3)$$

For the stress corrosion crack in the dual-phase steel which arrests under decreasing K conditions, the crack tip restraining force is exerted by the unbroken ligaments up to a distance  $c_{crit}$  behind the crack tip, at which point  $u = u_{crit}$ , where  $u_{crit}$  is the critical displacement necessary for the rupture of the austenite ligaments. Therefore from equations (2) and (3):

$$K_L = \frac{2\sqrt{2}}{\sqrt{\pi}} f\sigma_y\sqrt{c_{crit}} \dots\dots\dots(4)$$

$$u_{crit} = \frac{4\sqrt{2}}{\sqrt{\pi E'}} K_T\sqrt{c_{crit}} \dots\dots\dots(5)$$

Here  $K_T$  is the effective stress intensity experience by the crack tip. Eliminating  $\sqrt{c_{crit}}$  from equations (4) and (5).

$$K_L = \frac{f\sigma_y u_{crit} E'}{2K_T} \dots\dots\dots(6)$$

If the externally applied K is  $K_A$ , then

$$K_A = K_T + K_L \dots\dots\dots(7)$$

$$K_A = K_T + \frac{f\sigma_y u_{crit} E'}{2K_T} \dots\dots\dots(8)$$

At crack arrest,  $K_A$  is the measured threshold of the dual-phase steel and  $K_T$  is the intrinsic threshold of the martensite phase. The implication of equation 8 is that as the  $K_{TH}$  of the martensite decreases, the restraining K exerted by the austenite bridges should become increasingly significant. In other words the difference between the  $K_{TH}$  of the dual-phase steel and the conventional steel should increase as the yield strength is increased. This is in fact observed (Fig. 2).

It is instructive to apply the above equations to the crack tip situation shown in Fig. 5.  $c_{crit}$ , the distance over which the unbroken ligaments act, is about 300µm. The critical displacement  $u_{crit}$ , necessary for the rupture of the austenite should be of the same order as the thickness of the austenite and this is around 6µm. The volume fraction of austenite is 20%. Using these values in equation (5) the  $K_{TH}$  of the martensite is found to be 22 MNm<sup>-3/2</sup>. From equation (8) the value of  $\sigma_y$  is found to be 950 MPa which is a reasonable value for the constrained flow stress of a work-hardened austenite.

The martensite in the dual-phase steel has to be significantly harder than that in the conventional steel in order to obtain the same overall yield strength. The  $K_{TH}$  value of 22 MNm<sup>-3/2</sup> for the martensite in the dual-phase steel is considerably higher than would be expected from the results of the conventional steel. This improvement in  $K_{TH}$  arises from two sources. First the crack tip is physically shielded from the environment by the austenite ligaments. As the hydrogen generated by the corrosion reaction has to diffuse over a longer distance, the effective hydrogen concentration at the crack tip is reduced and this must result in an increased  $K_{TH}$ . Secondly, as shown in Fig. 5., the microcracks in the martensite invariably arrested in the austenite phase. This implies that the austenite has an additional crack arresting role.

The explanation for the unusual variation of stage II crack growth rate with strength is similar to that proposed for the threshold behaviour. In steels with conventional microstructures, the crack growth rate decreases with decreasing strength because of the need for increased hydrogen concentrations at the crack tip where the stresses are correspondingly less. In the case of the dual-phase steel, the shielding effect of the unbroken austenite ligaments reduces the hydrogen concentration in proportion to the distance over which hydrogen has to diffuse. This is related to  $c_{crit}$ , the distance over which the unbroken austenite ligaments extend. At high strength levels,  $c_{crit}$  is large and so the crack growth rates in the dual-phase steel will be correspondingly less than in the conventional steel. As the strength is decreased,  $c_{crit}$  decreases and the crack growth rate increases. Eventually, the growth rate in the dual-phase steel is expected to exceed that in the conventional steel because for a given yield strength, the strength of the martensite phase must be higher in the dual-phase steel. Such a cross-over in growth rate is indicated in Fig. 3.

CONCLUSIONS

A dual-phase steel in which islands of high strength martensite are surrounded by a network of stable austenite has been produced by extruding nickel-plated steel powder. It has been shown that with the dual-phase microstructure, it is possible to obtain very high strength combined with outstanding resistance to stress corrosion cracking in 3.5% NaCl solution. The superior stress corrosion performance is due primarily to the presence of the tough austenite, which when present in a continuous network is able to reduce both the effective stress intensity and the hydrogen concentration at the crack tip.

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