Effect of cold work on anodic polarization of low carbon steel

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Carbon steel nails prepared by deep drawing exhibit grains elongated in the direction of swaging. They are also characterized by high corrosion rates, as measured potentiodynamically in 0.1 M H_2SO_4. Normalization of grain dimensions and reduction in the corrosion rate are achieved through annealing. Treatment at 750° C for 2 h is effective in producing strain-free specimens with rounded grains. Extended heat treatment at this temperature causes the development of larger grains and the improvement in the corrosion behaviour of the alloy. "As-received" and strain-free specimens are subjected to controlled tensile or torsional cold work. In all cases deformation results in an increase in the susceptibility of the alloy to undergo attack. The rate of corrosion increases greatly when the deformed steel corrodes in Cl^- ion containing media. Both general and pitting corrosion are operative.

1. Introduction

The problem of corrosion of plastically deformed steels has been the subject of many studies [1–13]. Agreement between the results of the various workers is, however, far from being satisfactory. Thus, straining is considered to increase [1, 2, 6, 14], to decrease [3, 4] or to leave unaffected [4, 5] the corrosion rate. Similarly, cold work is considered by one group of researchers to affect only the potential range of the passive region [10], whereas others report a simultaneous increase in the corrosion current [11]. The effect of deformation is said to be potential dependent [13] and to depend on the previous heat treatment to which the deformed specimen is subjected [13] as well as on the pH value of the solution [11, 17]. Discrepancies in the information is also to be found regarding the consequences of cold work on pitting corrosion. Deformation is said to increase [9, 15] or retain unaltered [16] the number of pits, and to decrease pit size [9]. Under apparently similar conditions strain causes an increase in the number and total area of pits, as well as in the pitting corrosion current [1]. The growth rate of the pits is highest

at the initial stages of deformation and increases only slightly thereafter.

In view of this inconsistency in our knowledge, it appeared to be of value to re-examine, in a systematic manner, the role of cold work in the corrosion behaviour of low carbon steel in acid solutions. The study was carried out in a cyclic manner. Starting with a highly strained, hardened steel, the specimens were strain-relieved by annealing at various temperatures and for increasing times. The effect of the annealing treatment on the potentiodynamic polarization curves was recorded. Variations in the microstructure of the specimens, both in the longitudinal and the transverse direction were simultaneously noted. The fully annealed specimens were then subjected to controlled cold work, either as tensile or as torsional deformation. The polarization characteristics of the samples were measured in 0.1 M H_2SO_4, to establish the influence on general corrosion, as well as in the presence of increasing NaCl additions, to test for pitting corrosion suceptibility. The results of the present investigation revealed unequivocally that cold work increases the tendency of the steel to undergo

general corrosion and its tendency to undergo attack by pitting.

2. Experimental details

The electrodes used in the present study were ordinary carbon steel nails, 4 mm in diameter and had the following analysis (wt %): C 0.26, Mn 0.52, P 0.025, S 0.040 and Si 0.23, with the balance in Fe. The as-received specimens had an average Vickers microindentation hardness of 320. Annealing of the specimens was carried out in an electric furnace, in air, for 2 h at 200, 500, 600, 750 and 850° C, and at 750° C for periods extending to 10 h. The rate of cooling from the annealing temperature was 20° C min^{-1}. Sections of the annealed samples were taken in both the longitudinal and transverse directions, and the average grain diameter for 20 grains was measured under the metallographic microscope.

Strain-free specimens were obtained by annealing at 750° C for 2 h. These specimens were then subjected to varying degrees of cold work. Both tensile and torsional deformation were tested. In the first case the steel rods were exposed to 3, 5, 8 and 10% tensile deformation ($\Delta l/l$). Torsional deformation, on the other hand, was carried out by giving the rods 2, 5, 8 and 10 complete turns between the grips of a torsion machine. The extent of plastic deformation was considered to vary hand in hand with the number, N, of complete turns. The variation of the average grain size, the Vickers microhardness and the load–elongation characteristics of the specimens following these treatments were determined, and the results will be the subject of a separate communication.

For establishing the corrosion behaviour of the carbon steel rods, potentiodynamic polarization experiments were carried out using a Wenking Potentioscan type POS 73. A scanning rate of 5 mV sec^{-1} was always used, and polarization was directed from negative to positive potentials. The current/potential curves were recorded on Bryans XY Recorder 29000 A4. Experiments were carried out in 0.1 M H_2SO_4 free from and containing increasing concentrations of NaCl, as a pitting corrosion agent.

Electrodes of the steel rods, subjected to different heat and work treatments, were mounted in Araldite and soldered to thick copper wires for electrical connections. Only the cross-sectional areas of the specimens, of surface area of 0.126 cm^2, were exposed to the test electrolytes. Before being introduced into the electrolytic cell, the electrode surface was abraded successively with 0,00 and 000 metallographic emery paper, degreased with acetone and washed with running bidistilled water. The electrode was further subjected to pre-cathodization period of 5 min at -2 V vs SCE in the test solution, to reduce the pre-immersion oxide film present on its surface. Experiments were carried out at room temperature of 24 to 26° C.

3. Results and discussion
3.1. Effect of annealing temperature and time on the corrosion behaviour of the as-received steel

Photometallographs of the as-received samples, Fig. 1, showed the grains to be oriented in the swaging direction. The grains' length was 6 to 9 times their diameter; and the grain boundaries were diffuse and dim.

The specimens were subjected to heat treatment for two hours in a muffle furnace at different temperatures, to relieve them of their high strain. Annealing resulted in the diminution in grain length and the increase in grain diameter. The rate of the former exceeded, however, that of the latter. Changes in both directions depended on the annealing temperature. Treatment at 750° C produced practically equiaxed grains, Fig. 2. Beside affecting their dimensions, annealing resulted also in the development of more distinct grain boundaries. Above 750° C the grains increased in size and this was accompanied also by the initiation of carbide precipitation at grain boundaries. As will be presently shown, this phase change was associated with an increase in corrosion tendency of the alloy.

The potentiodynamic polarization curves of the "as-received" steel and of samples annealed for 2 h at different temperatures were recorded on 0.1 M H_2SO_4, and are drawn in Fig. 3a. Consideration of these curves reveals that the as-received sample started to dissolve anodically at about -0.50V vs SCE, curve 1. The dissolution current increased almost linearly to about $+0.8$V, passed through a flat maximum at $+1.0$V and then decreased gradually with potential. No proper passive region was recorded and at about $+1.8$V oxygen evolved on the electrode
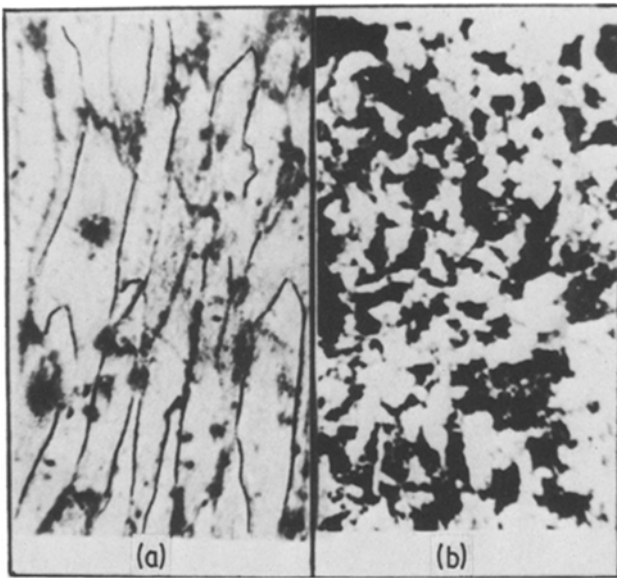
Figure 1 Photometallographic of the "as-received" carbon steel along the swaging direction. (a) longitudinal section and (b) transverse section.

in the transpassive region. Annealing for 2 h at 250° C promoted the dissolution of iron along the active range, and the critical current for passivation increased to almost double the value measured with the untreated sample. The active/passive transition was, however, better defined and the passive current decreased much below that of the unannealed specimen. Careful examination of the photomicrographs of the steel annealed at 250° C failed to reveal the presence

of any unusual features which might account for the high dissolution rate recorded along the active region. The grain dimensions were practically the same as those of the unannealed specimens. Similarly, the annealing temperature was much too low to affect cementite of pearlite formation. We assume, therefore, that heating at 250° C initiated and promoted the diffusion of dislocations from the inside of the metal to the surface. Since a structural fault at the metal surface is
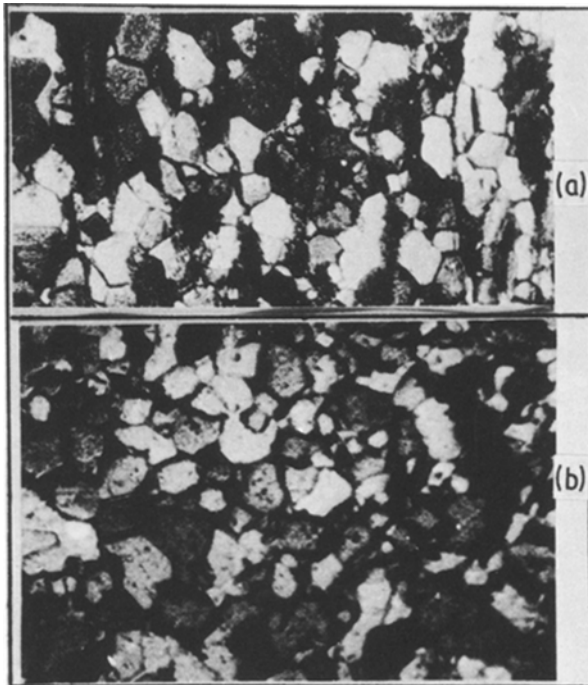

Figure 2 Photometallograph of the carbon steel after annealing at 750° C for 2 h. (a) longitudinal section and (b) transverse section.
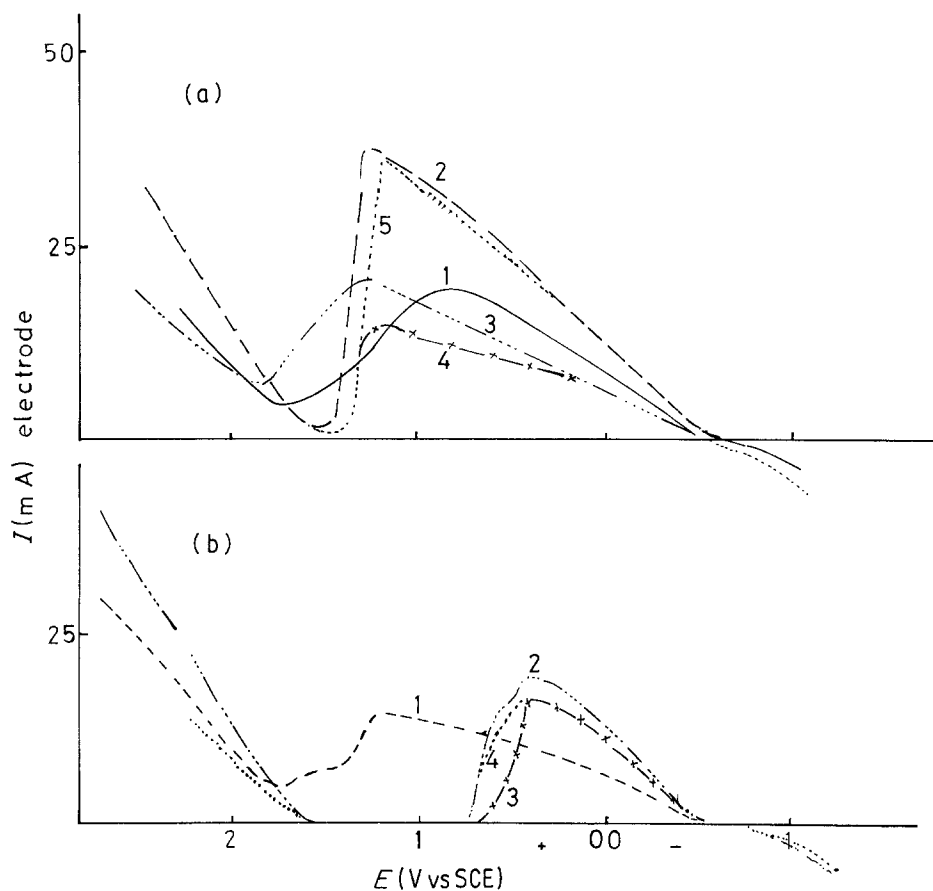
Figure 3 (a) Effect of annealing for 2 h at different temperatures on the potentiodynamic polarization curves of carbon steel in 0.1 M H_2SO_4. Curve 1 as-received, curve 2 250° C, curve 3 500° C, curve 4 750° C and curve 5 850° C. (b) effect of annealing time at 750°C on the potentiodynamic polarization curves of carbon-steel in 0.1 M H_2SO_4. Curve 1 2 h, curve 2 4 h, curve 3 8 h and curve 4 10 h.

likely to present a centre of high activity, one would expect a corresponding increase in the dissolution rate.

Although an increase in annealing temperature was expected to accelerate the migration of imperfections to the metal surface, and hence to increase the dissolution rate, the reverse effect was actually recorded. Reference to curves 3 and 4 of Fig. 3a reveals that annealing at 500 and 750° C for 2 h resulted in a noticeable reduction in the rate of metal dissolution in the active range. This behaviour can be readily understood when one takes into consideration that the rise in temperature diminishes the imperfection density be eliminating the cause of their occurrence, namely, internal strains. Evidence for strain-relief was noted from the changes in the dimensions of the grains. When annealing was carried out at 850° C a large increase in the corrosion tendency of the steel was recorded. The potentio-

dynamic polarization curve rose once again and coincided almost practically with that for the sample heated at 250° C. As was stated before, the photomicrographs of the alloy treated at 850° C revealed the start of carbide precipitation along grain boundaries. This accounts for the high dissolution rates recorded in polarization experiments. For this reason, strain-relief treatment of the test samples was limited to 750° C. At this temperature, the microstructure of the alloy consisted of pearlite colonies embedded in a ferrite-grain matrix.

Next, the effect of the annealing time at 750° C on the corrosion characteristics of the alloy was considered. The curves of Fig. 3b represent the potentiodynamic polarization behaviour in 0.1 M H_2SO_4 for specimens annealed for 2, 4, 8 and 10 h at 750° C. As is evident from the curves, an increase in the heat-treatment time from 2 to 4 h improved in many ways the corrosion

characteristics of the alloy. First, the potential range of active dissolution was considerably reduced. Second, the transition from the active to the passive states was better defined, and finally, the passive current became negligibly small and extended over a range of approximately 1 V. Extension of the annealing time beyond 4 h brought about a slight decrease in the critical current for passivation, but left unaltered the other features of the polarization curves. Metallographic examination of the specimens revealed that the grain diameter increased hand in hand with the time of annealing. After 2, 4, 6, 8 and 10 h of annealing at 750° C, the average grain diameter amounted to 5.0, 5.5, 5.7, 6.2 and 6.5×10^{-2} mm, respectively. The corresponding Vickers microhardness values were 195, 191, 188, 184 and 180, respectively. The "as-received" steel had an average grain length of 14.5×10^{-2} mm and an average grain diameter in the transverse direction of 2.8×10^{-2} mm. Its Vickers hardness was 320. The gradual changes in the grain dimensions through the rise in the annealing temperature, and the increase in the grain dimension through the increase in annealing time at 750° C, as well as the reduction in the microhardness of the specimen, are all indications of strain-relief of the high cold work to which the as-received specimens were subjected during manufacture. This, as has been shown above, is accompanied by the improvement of the corrosion characteristics of the alloy. One cannot, therefore, escape the conclusion that the high corrosion rate of the "as-received" alloy was the result of the severe cold work to which the steel was subjected. This conclusion is strongly substantiated by the results of experiments described in the following section.

3.2. Effect of controlled cold work on the corrosion behaviour of carbon steel

Metallographic examination and microhardness measurement reported in the previous section both revealed that the plastically deformed steel was strain-relieved by annealing at 750° C for 2 h. The originally elongated metal grains acquired a normal equiaxed form. In the meantime, potentiodynamic polarization experiments showed an improvement in the corrosion characteristics of the alloy, which varied hand in hand with the temperature and time of heat treatment. It was therefore inferred that the cold work

reduced the passivity and enhanced the anodic dissolution of the samples. To give experimental support on this conclusion, a study was carried out on the effect produced on the potentiodynamic polarization curves when subjecting the strain-relieved specimens to controlled cold work. Cold work was introduced in the form of either percentage tensile deformation or in the form of torsion.

The curves of Fig. 4 represent the potentiodynamic polarization behaviour of the "as-received" steel in 0.1 M H_2SO_4, after being subjected to different degrees of tensile deformation. Cold work affected the polarization curves in a number of ways. First, the dissolution current recorded along the active region increased noticeably above that of the untreated sample. Dissolution was almost doubled with the first strain 3%. Further increase in the deformation brought about only a slight additional increase in the activity. Second, with low tensile deformation ($\leqslant 5\%$) the active/passive transition was sharp and well-defined; and the passive current density was considerably lower than that developed by the as-received specimen. The curves were characterized, however, by a limited passive potential domain. On the other hand, samples which received 8 and 10% deformation exhibited exceptionally high corrosion currents in the passive range, which increased in proportion to the degree of strain. With these last samples, current oscillations were also recorded in the transpassive range. These oscillations indicate the presence of an imperfect and/or discontinuous oxide film on the surface of the alloy. It is of interest to note that within ± 30 mV, and in agreement with the results of Finely and Myers [10], the corrosion potential (where $i_a = i_c$) is practically independent of the extent of cold work to which the electrode was subjected.

Curves exhibiting the same general features as those of Fig. 4 were also obtained when the steel was annealed at 500 and 750° C, for 2 h, prior to the application of the plastic tensile deformation. These experiments revealed that the effect of one and the same degree of tensile deformation on the active dissolution of the alloy depended on the amount of strain still retained in the specimen. The higher these strains were, the larger was the dissolution current of the plastically deformed electrode.
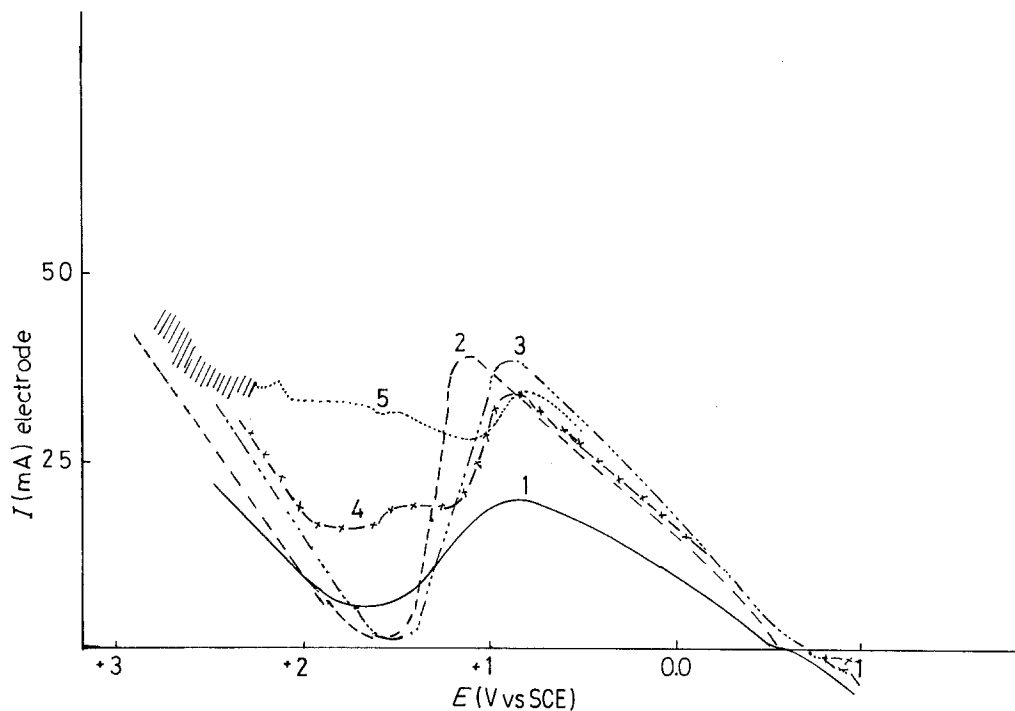
Fully strain-relieved steel specimens were

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Figure 4 Effect of tensile deformation on the potentiodynamic polarization curves of the as-received carbon steel in 0.1 M H_2SO_4. Amount of strain $\Delta l/l$: curve 1, 0%, curve 2, 3%, curve 3, 5%, curve 4, 8% and curve 5, 10%.

prepared by annealing at 750° C for 6 h. These were later subjected to various degrees of tensile plastic deformation and their potentiodynamic polarization curves in 0.1 M H_2SO_4 were determined. Different samples given the same treatment were used. The results of this set of experiments are presented by the curves of Fig. 5. Cold work increased the susceptibility of the alloy towards corrosion in two different ways, but the changes did not follow an ordered sequence. Thus, for example, deformation broadened the potential range for active dissolution and reduced that of the passive region. This effect did not follow, however, the degree of tensile deformation. On the other hand, cold work brought about an increase in the corrosion current in the active region which, again, varied nonsystematically with the extent of deformation. We are unable to advance a reasonable explanation for this unusual phenomenon. It should be stated, however, that this behaviour was quite reproducible, and as will be presently shown, it was also noted when deformation was introduced in the form of torsion. In this respect our results differ from those of Chance [13], who reported that the length of the passive region decreased and the passive current density increased in proportion to the extent of

torsional deformation. This is not, however, the only difference between the results of the two sets of measurements. Chance [13], who carried out his polarization experiments in 0.6 M ammonium nitrate solution, also reported that cold work did not significantly affect the region of active dissolution. Cold work was also introduced to the carbon steel in the form of torsional deformation by twisting rods, measuring 6 cm, 2, 5, 8 and 10 times on a torsion machine. Electrodes were prepared in the usual manner and their corrosion behaviour was established in 0.1 M H_2SO_4. The curves of Fig. 6 represent the effect of increased torsional deformation on the polarization characteristic of the steel, which was pre-annealed for 2 h at 500° C. Similar to the case of tensile deformation, torsion greatly increased dissolution along the active region. The effect of the first three turns was comparatively larger than that of the subsequent two. The transition from the active to the passive states was quite abrupt and the passive currents were noticeably smaller than that of the specimen not subjected to twisting. Further increase in the number of turns resulted in the decrease in the critical current for passivation and the specimen which received 10 turns gave the lowest dissolution current. Long
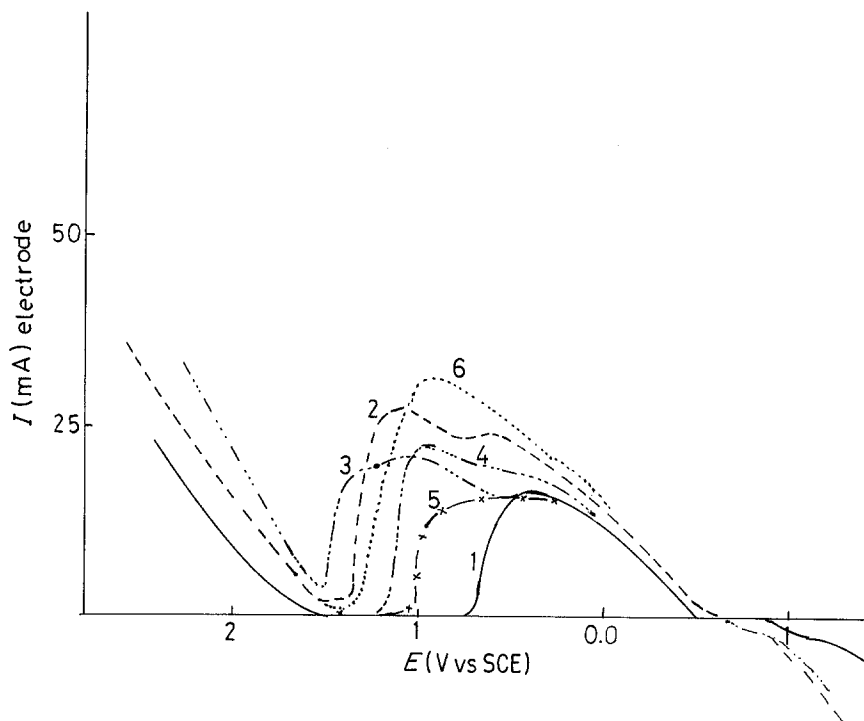
Figure 5 Effect of tensile deformation on the potentiodynamic polarization curves of carbon steel annealed at 750° C for 6 h. Polarization in 0.1 M H_2SO_4. Amount of strain $\Delta l/l$: curve 1 0%, curve 2 3%, curve 3 4%, curve 4 5%, curve 5 6% and curve 6 10%.
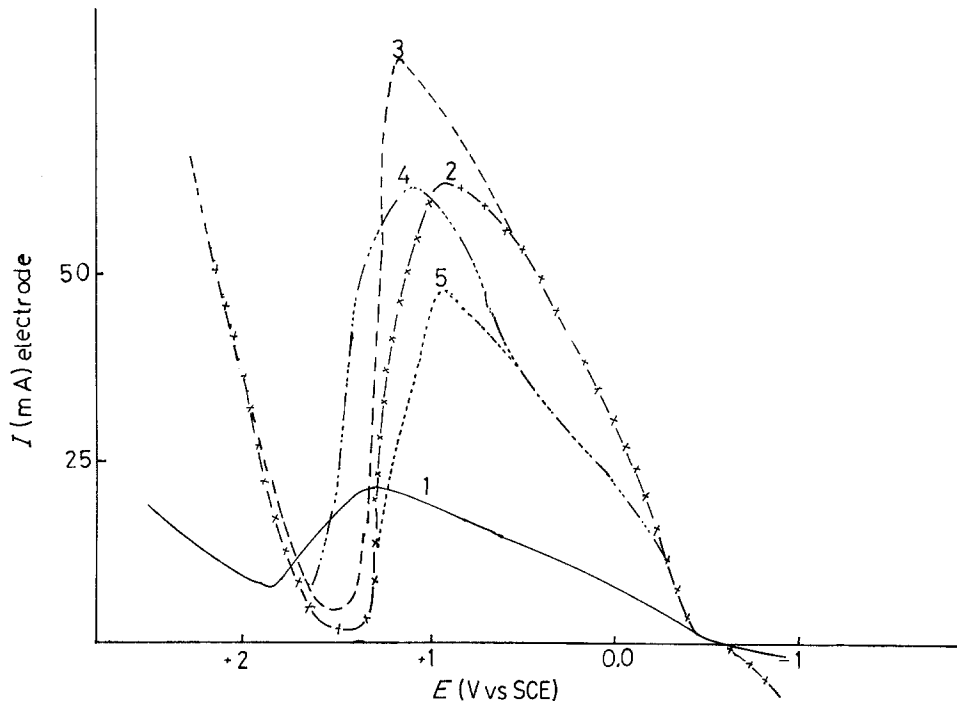

Figure 6 Effect of torsion deformation on the potentiodynamic polarization curves of carbon steel annealed for 2 h at 500° C. Polarization in 0.1 M H_2SO_4. Numbers of turns curve 1, 0, curve 2, 2, curve 3, 5, curve 4, 8 and curve 5, 10 turns.

and Uhlig [17] similarly reported that low carbon steels which were subjected to severe cold work showed increased corrosion resistance to nitrate solutions and they reasonsed that grain boundary continuity of precipitated carbon was disrupted by deformation. The curves of Fig. 6 also show that the decrease in active dissolution was accompanied by a shortening in the passive potential range and a slight increase in the passive current. The two last effects indicate that the plastic deformation induces the breakdown of passivity of the alloy.

Polarization curves similar to those given in Fig. 6 were also obtained when torsional deformation was applied to the "as-received" alloy and to samples which were heat treated at 600 and 750°C for 2h. One common feature of these experiments was the decrease in the corrosion current of samples subjected to a large number of twists and the subsequent rise in their passivation currents.

3.3. Effect of Cl⁻ ion and cold work on the corrosion behaviour of carbon steel

Chloride ion increases the attack on steels in two distinct ways. With easily corroding alloys, the aggressive ion promotes the dissolution of iron along the active region, and raises the current in the domain of passivity [18]. With stainless steels, on the other hand, the action of Cl⁻ ion predominates in the passive range. Attack is limited to small pits, and develops at definite potentials depending on the concentrations of the halogen ion and of the supporting electrolyte, as well as on the ratio thereof [19]. In view of the fact, that cold work was found to reduce the corrosion resistance of carbon steels, it appeared of interest to establish how this would be aggravated by the Cl⁻ ion and, vice versa, how the Cl⁻ attack would be intensified through cold work. Agreement between the results of the various authors in this connection is lacking [9, 15, 16, 20, 21].

The curves of Fig. 7 represent the effect of increasing concentrations of the Cl⁻ ion on the polarization behaviour of the "as-received" carbon steel in 0.1 M H_2SO_4. The presence of as little as 1×10^{-4} M Cl⁻ in solution caused an increase in the dissolution current, and the extension of the domain of activity towards more postive potentials. In the meantime the passive current increased appreciably above that measured in Cl⁻-free solutions. Passivity completely disappeared in the presence of the Cl⁻ ion $\geqslant 1 \times$
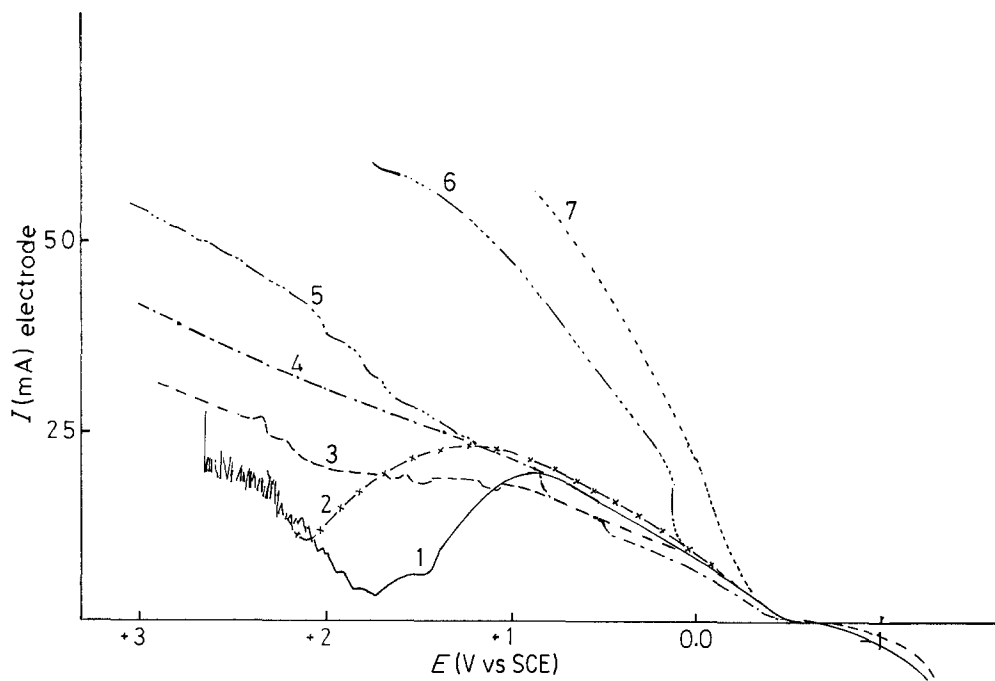

Figure 7 Effect of Cl⁻ ion concentration on the potentiodynamic polarization curves of as-received carbon steel in 0.1 M H_2SO_4. [Cl⁻] for curve 1 is 0, curve 2, 1×10^{-4}, curve 3, 1×10^{-3}, curve 4, 3×10^{-3}, curve 5, 1×10^{-3}, curve 6, 3×10^{-1} and curve 7, 1 M NaCl.

10^{-3} M, and the polarization curves assumed the form of linear plots whose slopes varied in direct proportion to the Cl^- content of the solution. Viewed after the end of the polarization experiments the electrodes exhibited rough surfaces indicative of severe attack. In concentrated halide solutions a few large pits were also seen. The curves of Fig. 7 also show that the corrosion potential depended little on the Cl^- concentration; a result which substantiated the conclusion that the aggressive ion was specifically adsorbed on the metal surface at a potential more negative than E_{corr} [18]. The curves of Fig. 8 represent the potentiodynamic polarization

behaviour (in the presence of 1×10^{-3} and 1×10^{-2} M NaCl, respectively, of the "as-received" specimens which were subjected to different tensile deformations). Both sets of curves demonstrate clearly the conjoint action of Cl^- ion/cold work on the corrosion of the steel in aqueous solutions. Thus, in the presence of one and the same concentration of the aggressive anion, cold work raised the dissolution current noticeably above that of the already highly swaged specimen. Although the effect progressively increased with the percentage elongation, the effect of the initial deformation was always larger than that of the subsequent, numerically larger work. Further,
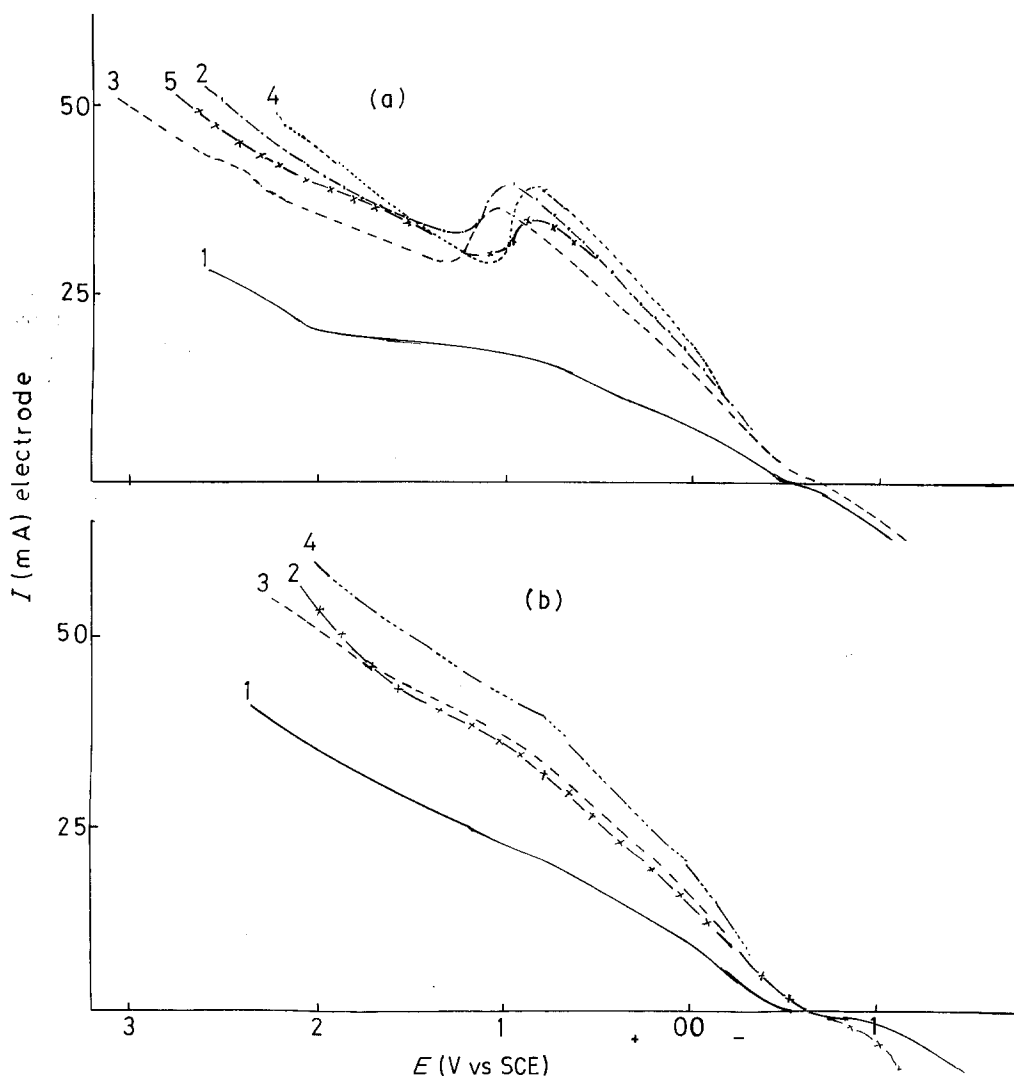

Figure 8 (a) Effect of tensile deformation of as-received carbon steel on the potentiodynamic polarization curves in 0.1 M H_2SO_4 + 10^{-3} M NaCl. Amount of strain $\Delta l/l$: curve 1, 0%, curve 2, 3%, curve 3, 5%, curve 4, 8% and curve 5, 10%. Effect of tensile deformation of as-received carbon steel on the potentiodynamic polarization curves in 0.1 M H_2SO_4 + 10^{-2} M NaCl. Amount of strain $\Delta l/l$: curve, 1, 0, curve 2, 3%, curve 3, 5% and curve 4, 8%.

for equally strained samples, the attack is greater the greater the Cl⁻ ion concentration. Curve similar to those of Fig. 8 were obtained in solutions of other Cl⁻ contents and with electrodes in which the deformation was introduced torsionally.

Experiments were similarly carried out on specimens which were fully strain-relieved through annealing at $750°$ C for periods extending to 6 h. These were then tested in Cl⁻-containing solutions of different concentrations, either as such, or after being subjected to tensile or torsional deformation of various degrees. The results of this extended study revealed that the strain-relieved alloy was quite sensitive to cold work and/or to traces of the Cl⁻ ion. This is well demonstrated by the curves of Fig. 9. Curve 1 shows the corrosion behaviour in 0.1 M H_2SO_4 of the alloy after being annealed at $750°$ C for 2 h. Curve 2 is for the same alloy after receiving 5 turns on the torsion machine. As expected, cold work increased the dissolution rate of the material. The other curves of Fig. 9 were obtained with the deformed electrode in solutions containing minute additions of the aggressive anion. Below 1×10^{-3} M Cl⁻, the dissolution current progressively evolved in proportion to C_{Cl^-}. In the presence of 3×10^{-3} M Cl⁻, the passive range almost disappeared and the current associated with it rose to a high

value. The specimen suffered severe attack. Further increase in the Cl⁻ content of the solution gave rise to polarization curves in which the current varied almost linearly with the applied potential.

4. Conclusions
From the results of the present investigation the following conclusions are drawn:

1. Deformed carbon steel nails prepared by deep drawing exhibit high corrosion rates. Annealing relieves the internal strains and normalizes the dimensions of the grains. The effects depend on the temperature and the treatment time. Equiaxed grains are obtained by annealing at $750°$ C for 2 h. Larger grains are produced when treatment is extended to longer times. Annealing considerably improves the corrosion characteristics of the alloy. One can safely infer that the cold work, to which the steel has been subjected during manufacturing, is detrimental to its corrosion resistance.

2. When "as-received" or annealed specimens are subjected to cold work in the form of tensile or torsional deformation their resistance to anodic attack is reduced. The effect depends on the magnitude of lattice imperfection present in the sample before deformation. The effect of the
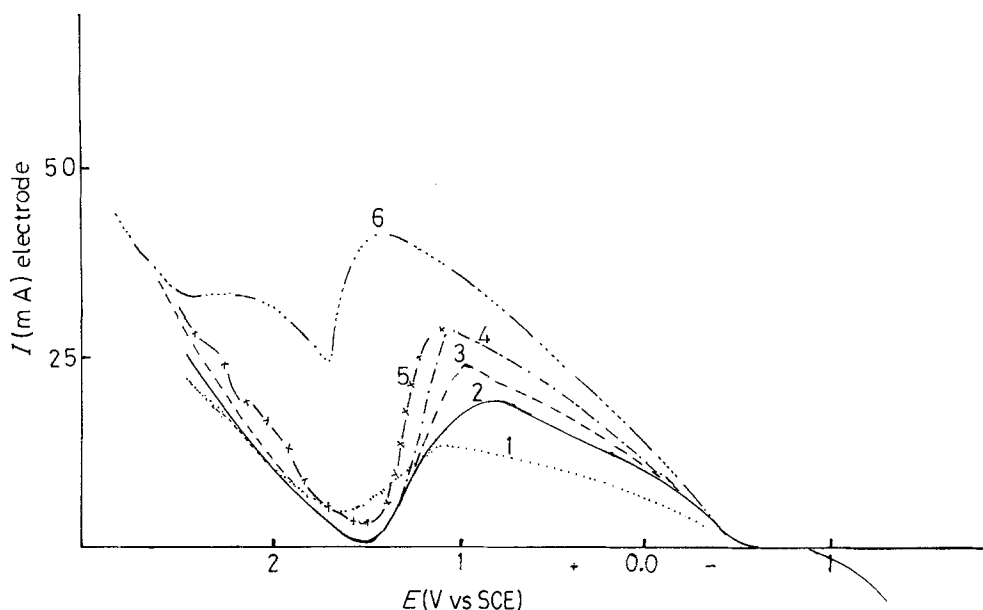

Figure 9 Effect of Cl⁻ ion concentration on the potentiodynamic polarization curves of strain-relieved and twisted carbon steel. Curve 1 strain relieved steel in 0.1 M H_2SO_4. Curve 2 same as in curve 1, steel deformed by 5 turns. Curve 3 same as curve 2 and in presence of 1×10^{-4} M Cl. Curve 4 same as curve 2 and in presence of 3×10^{-4} M Cl. Curve 5 same as in curve 2 and in presence of 1×10^{-3} M Cl. Curve 6 same as curve 2 and in presence of 3×10^{-3} M Cl.

first small degree of deformation is more pronounced than of subsequent larger deformation. Excessive cold work appears; however, to slightly improve the corrosion resistance of the steel.

3. Chloride ions increase the corrosion rate of the steel, whether it is in the "as-received" or the annealed state. Dissolution varies hand in hand with the aggressive ion content of the solution. Attack starts generally in the presence of small concentrations of the Cl^- ion, but produces large pits at higher contents. Cold work intensifies the two types of attack in proportion to both the extent of deformation and the concentration of the aggressive anion.

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