A REVIEW OF THE EFFECT OF COLD-WORK ON RESISTANCE TO SULPHIDE STRESS CRACKING

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ABSTRACT

The specific problems associated with the use of steels in H_2S-containing environments have been extensively documented. Perhaps the most severe problem encountered in such environments is the occurrence of sulphide stress cracking. Years of industrial experience and laboratory tests have helped define safe conditions for the use of C-Mn steels in sour service. However, whether these conditions remain for cold-worked material is not clear for the literature. The present paper presents a critical literature survey on the effect of plastic strain applied prior to service, on the SSC resistance of C-Mn steels. Based on data published over the past 50 years, this review considers the problem from two points of view. Firstly, documents are reviewed which discuss results of SSC tests of plastically strained material. Secondly, results are reviewed which discuss the effect of cold work on hydrogen embrittlement in a more general manner. Conclusions are drawn on the expected severity of the impact of strain on SSC resistance, and areas are identified where further experimental work is required.

Keywords: sulphide stress cracking, cold-work, plastic strain, reeling, hydrogen embrittlement

INTRODUCTION

The possibility that cold work affect the resistance to sulphide stress cracking is not unrecognised. Both references [1] and [2] underline the detrimental effect of cold work on the performance of C-Mn steels in sour conditions. Reference [1] in particular, indicates clearly that cold working may render the material susceptible to SSC, even with a hardness under 250 HV. Both references suggest that cold-working above 5% deformation should be followed by heat-treatment. It is therefore implied that plastic deformation under 5% strain should have no significant impact on the resistance to sulphide stress cracking of C-Mn steels. In particular, there is no revision of the maximum hardness criterion of 250 HV. A small pilot study carried out at TWI suggested that plastic strain could have an adverse effect on the resistance of welds to SSC, even when the hardness remained under 250HV. It is indeed possible that with hardnesses close to 250HV, less than 5% strain could lead to a risk of SSC.

While reference [3] indicates that 'the deleterious effect of cold work on resistance to SSC is well known', most research publications indicate that, while well known, the effect remains poorly understood [4, 5].

One of the possible sources of confusion lies what is meant by 'effect of strain'. A number of studies have been concerned with the impact of straining during exposure to sour environments [4]. In the slow strain rate test (SSRT), for example, tensile samples are tested at strain rates about 10^{-7}-$10^{-4}s^{-1}$ in a sour environment. There is no disagreement, in this case, that straining has a considerable impact on ductility and rupture stress. This is, however, of little relevance to the present study. Similarly, the effects of prior cold work on SSRT or similar tests are not directly relevant. Of interest are studies highlighting the influence of prior cold work on C-Mn steels performance in sour environments under static loading below the yield stress.

The present literature search has been divided in two parts. In a first part, results that are directly relevant to the SSC resistance of cold-worked materials are considered. In a second part, considerations are given to the mechanisms by which SSC occurs. Sulphide stress cracking is a particular occurrence of hydrogen embrittlement (at least for the alloys considered, and in the test conditions envisaged), where the hydrogen is generated as part of the cathodic corrosion reaction. In fact, some authors [6] have used the term 'hydrogen embrittlement' to refer to SSC. The effect of cold work can therefore be approached from different angles: effect of cold work on hydrogen absorption on one hand and effect of hydrogen content on mechanical properties of the material on the other hand.

One of the difficulties in reviewing the effect of a particular parameter is that other parameters are often not kept identical (environment, straining method, loading method, material chemistry). Results are therefore often not directly comparable. In addition, there are various methods to assess the performance of a given material in sour service, the outputs of which are not necessarily comparable. For example, one method applied in a number of early studies (NACE TM0177 method B also referred to as Shell Sc) consists of testing samples in three point bend jigs, and estimating a 'critical stress' from the deflection of the sample. This estimation neglects the stress concentration resulting from the presence of two small holes drilled in the samples. The quantity is therefore not an accurate measure of the stresses within the sample, and is without meaning when samples are loaded above their yield stress. This method has only been used for comparison of different materials. Other studies have reported the load as a percentage of the yield stress, not always specifying whether the yield stress is that before or after cold working. For these reasons, a detailed account of results collected is presented below, followed by a discussion.

RESULTS OF DIRECT RELEVANCE

Review

To assess the impact of rotary straightening of pipes, Baldy [7] carried out tests on undeformed and cold-worked N-80 steel, of composition indicated in table 1 and using three different material conditions leading to different tensile properties: normalised ("N"), normalised and tempered one hour at 621 °C ("NT1"), and normalised and tempered at 650 °C ("NT2"). The hardness of the normalised material was 24 HRc (~264 HV), which is higher than would be expected from a fully normalised microstructure for a material of this composition (205 HV, estimated with Stecal [8]). Therefore, whilst the material was clearly not fully martensitic in the normalised condition, it was also probably not fully pearlitic. This is also confirmed by the marked effect of tempering, which lowered the hardness of the material by as much as 16 HRc.

Table 1: Composition of the steels used in investigations by Baldy [7], Asahi and Ueno [9] and Asahi *et al* [10].

Elt / wt%	C	Mn	P	S	Si	Mo	Others	Ref.
	0.44	0.26	0.013	0.026	0.26	0.24	-	[7]
	0.25	0.52	0.006	0.001	0.11	0.44	0.03Nb, 0.03Al, 0.02Ti, 0.0035N, 0.001B	[9]
	0.12	1.12	0.009	0.002	0.18	-	0.03Nb, 0.024Al, 0.0034N	[10]

Baldy used tensile samples loaded at a constant stress in modified creep testing machines. The samples were placed in a solution of 0.5% acetic acid in distilled water through which a 50/50 mixture of H_2S and CO_2 was continuously bubbled. Prior to the sulphide stress cracking tests, some of the samples had been strained to 1% strain in tension. The results indicated that 1% cold work was sufficient to lower the load carrying capacity of N-80 steels significantly.

The actual results from Baldy do not report a threshold stress; instead, the occurrence of failure was recorded for different values of applied stress (typically four samples were tested at the same stress value). Using these data, the present author inferred a threshold stress (highest stress at which no failure occurred in 1000 h) for the different material conditions tested. The interpretation, however, is not straighforward. Yield stress (YS), ultimate tensile strength (UTS) and elongation are provided, though only for the unstrained conditions. As neither full tensile results nor YS or UTS for strained samples are available, the actual YS of the strained material is unknown.

The present author estimated the yield stress after 1% straining using two methods: in the first place, the stress at 1% strain was estimated assuming a linear strain hardening between YS and UTS over the known elongation. This is likely to underestimate the strain hardening and therefore provided a lower bound. In the second place, the stress-strain curves were modelled using:

$$\sigma = \sigma_0 + k\varepsilon^n \qquad (1)$$

where σ is the stress, ε the strain and k and n constants. Two values of n were used (0.10 and 0.15), thought to be the lowest and typical values respectively for steels with strength around 600 MPa [11]. Higher values of work hardening were obtained with $n = 0.10$ and it was therefore considered reasonable to assume these values would correspond to an upper bound. As underlined in reference [11], the parameter σ_0 should in principle be equal to the yield stress, but a better fit is often obtained with values of σ_0 below the yield stress. Therefore, both k and σ_0 were calculated to obtain a 0.2% proof stress equal to the yield stress values reported, and a stress equal to the UTS at the final elongation.

The summary of the results are given in table 2. Values of stress at 1% strain, obtained for $n = 0.10$, were always larger than those obtained with $n = 0.15$. The lowest values were those obtained from the linear interpolation.

Table 2: Strength of the material tested by Baldy [7] in different heat-treatment conditions, and estimated strength after straining, using two methods.

Material	N	NT1	NT2
YS /MPa	624	575	525
$\sigma_{1\%,\mathrm{min}}$	639	584	533
$\sigma_{1\%,\mathrm{max}}$	694	624	592

Asahi and Ueno [9] have carried out a similar study on a seamless pipe material of yield stress around 700 MPa. Tests were NACE TM0177-90 method A (constant load tensile tests) in NACE TM0177 solution A (5% NaCl + 0.5% acetic acid, saturated with H_2S). The threshold stress was defined as that for which there was no failure after 720 h (it is not known, unfortunately, at which stress intervals tests were carried out, and therefore it is difficult to estimate the uncertainty that might exist on the value of the threshold stress). For prestrained specimens, deformation was by tensile straining. The authors varied the strength of the material by varying the tempering temperature between 640 and 720 °C, and the samples tempered at 700 °C were strained to 3, 6 and 10% prior to SSC testing. In this case, the authors did report the yield stress of the strained material.

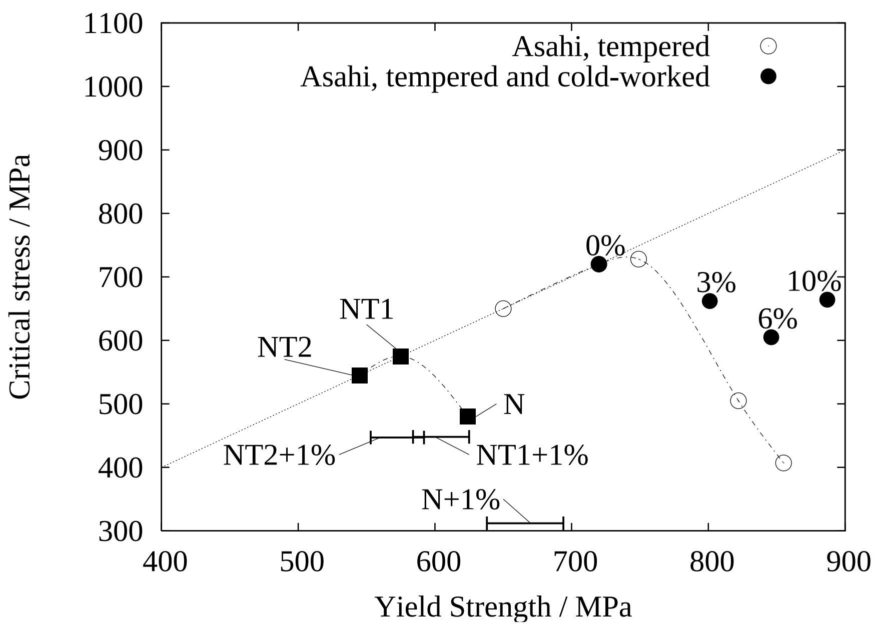

Figure 1: The critical stress SSC of for N-80 and Asahi's steels in various conditions. In Baldy's work [7], the strongest material was only normalised, while materials of lower strength were normalised and tempered. The yield stress of the strained material was estimated by the present author, using two methods which provide lower and upper bounds for possible values. The critical stress was taken, by the present author, as being the highest stress at which no failure occurred in 1000h. Asahi and Ueno's work [9] provide threshold stress and yield stress in strained conditions.

Figure 1 compares the result of both studies by showing the effect of varying the yield strength through tempering (variations outlined in dashed lines) and through work hardening (individual points with indication of the degree of work-hardening). As can be seen, while in both cases, there is a detrimental effect of strain on the threshold stress, the conclusions differ significantly. Baldy's work indicates that the effect of strain on SSC susceptibility is greater than that of the corresponding increase in strength alone. For example, the critical stress for sample NT2 following straining to 1% (indicated in figure 1 as NT2+1%) is significantly lower than that of sample NT1; however the estimated yield stress of sample NT2+1% is approximately equal to the that of samples NT1.

Although Asahi and Ueno [9] concluded that the detrimental effect of cold-work on SSC resistance was probably caused by an increased in yield stress, their results indicate that the effect of strain on SSC susceptibility is less than that of the corresponding increase in strength. In this sense, their conclusions are opposite to those of Baldy. As can be seen in figure 1, the points for strained material lie above the curve for the materials whose strength was varied by changes in the tempering treatment.

Figure 1 also suggests a behaviour whereby the threshold stress firstly increases with increasing yield strength, but decreases beyond a given value which perhaps depends on the material under consideration. However, it should not be assumed that the threshold stress equals the material yield stress in this region. This is possibly only a consequence of the fact that the investigators did not carry out tests for stresses above the yield stress. Indeed, investigations where loads have been allowed to exceed the yield stress have demonstrated threshold stresses above the as-received yield stress [12]. Nevertheless, it appears as if below a given value, the SSC threshold stress is at least equal to the as-received yield stress.

Further results by Asahi *et al* [10] appear to illustrate a rather different behaviour for a lower strength steel (450 MPa, composition given in table 1). In this case, the threshold stress was below the as-received yield stress. However, following cold-working by tensile straining, the threshold stress increased and was found to be at least equal to the new yield stress (figure 2). These results are

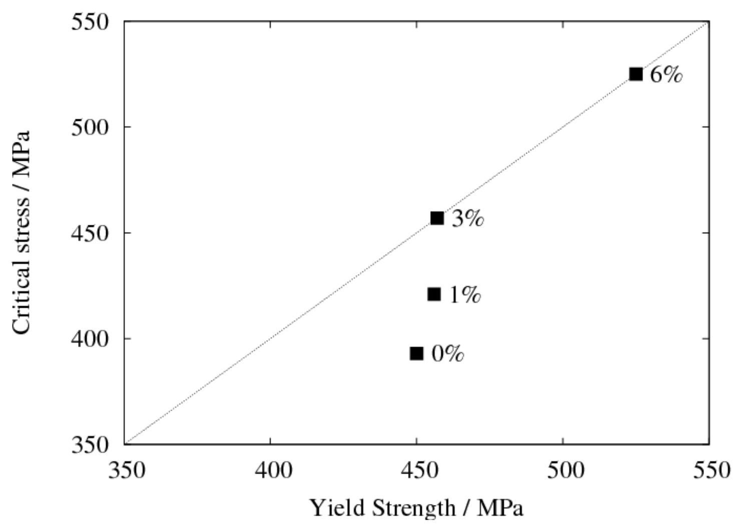

Figure 2: The critical stress for the SSC of a low strength steel as investigated by Asahi *et al* [10]. Cold work appears to result in an increase of the critical stress.

surprising for a number of reasons. Firstly, the authors demonstrate that the material investigated has a yield point, with a Lüders strain about 3%. It is therefore surprising that the material strained to 1% plastic strain behaves differently from both the as-received material and the material strained to 3%. It is reasonable to expect that the material strained to 1% will exhibit regions strained to 3% plastic strain and regions with little or no deformation. The cracking resistance should then be dictated by the weakest regions, which, according to the results of the authors, are the unstrained one. One would therefore expect the critical stress to be identical to that in the as-received samples.

Unfortunately, as is often the case in similar studies, the authors do not report the details of their test programme and it is difficult to comment on the significance of the increase compared to the expected accuracy with which the critical stress is estimated. It seems reasonable however, to suggest that the increase is well within the uncertainty typically accompanying the determination of the critical stress. Secondly, that the increase of strength should result in an increase of critical stress is opposite to virtually all other results identified in this review.

Treseder and Swanson [13] investigated the effect of cold work on SSC resistance for three API steel grades J55, C75 and X52. In this case, cold work was applied by cold rolling to 4, 8, 16 and 32% thickness reduction. Chemical composition was only provided for the C75 tubing material (table 3). The tests consisted in placing three point bend specimens, with two drilled holes, in a

Table 3: Composition of the tubing steels used in by Treseder and Swanson [13]. (*) not indicated in the reference, standard requirements are given for reference.

Grade	C	Mn	P	S	Si	Mo	Ni	Cr	Cu
C75	0.45	1.62	0.02	0.014	0.20	0.19	0.014	0.012	0.024
X52 (*)	< 0.20	< 1.40	< 0.030	< 0.030	-	-	-	-	-
J55 (*)	< 0.36	< 1.60	< 0.030	< 0.030	-	-	-	-	-

solution of 0.5% acetic acid in distilled water, saturated with H_2S (Shell Sc test). In this test, of four weeks duration, the stress in the outer fibre of the specimen was estimated from the deflection of the specimen. As discussed earlier, because of the presence of stress concentrators (holes) and because, in this procedure, the stress is estimated from the deflection of the beam whether in the elastic or plastic strain regime, this stress has little physical meaning, making the test useful only for comparative studies. From a number of experiments at different values of stress, the Sc value is

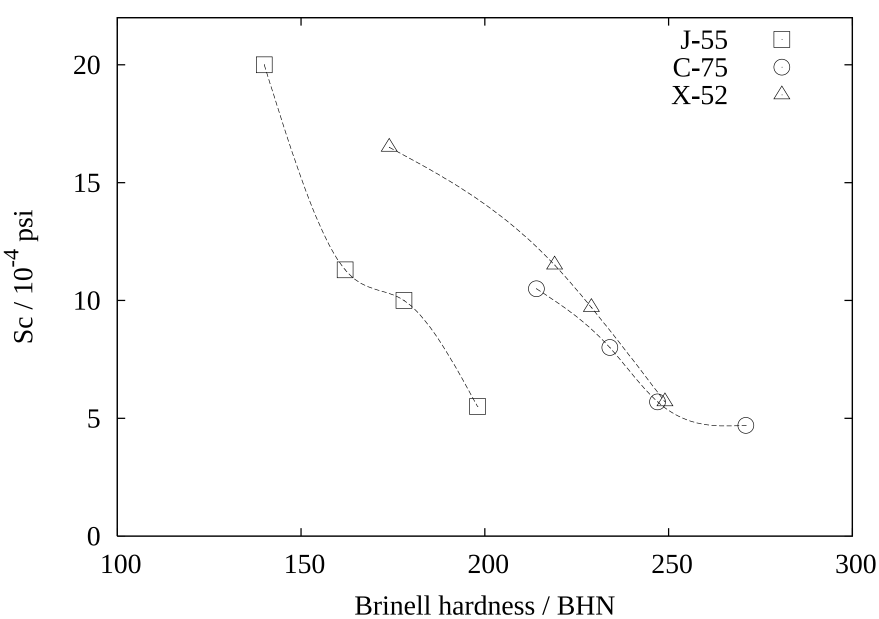

Figure 3: The effect of hardness increase (caused by cold working), on the SSC susceptibility of three API grade steels. Increases in hardness were obtained by cold rolling to 4, 8, 16 and 32% thickness reduction. After Treseder and Swanson [13].

determined, where Sc is the estimated stress giving a 50% probability of failure. Prior deformation was by cold rolling. The results obtained by these authors are shown in figure 3. According to the authors, a value of Sc=10 ($\times 10^4$ psi) is the lower limit for acceptability and is the basis of the hardness limit of 235 HBN ($\sim$ 247HV) recommended by NACE (at that time). In this case however, it was shown that some of the cold-worked materials had values of Sc under 10, although their hardness was below 235 HBN.

Dvoracek [14] carried out tests on P-110 grade heat-treated (quenched and tempered) to different strength levels and cold-worked. The composition of the material is given in table 4. The tests

Table 4: Composition of the P110 casing material used by Dvoracek [14].

Elt	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Al
wt%	0.45	1.18	0.009	0.028	0.32	0.03	0.02	0.08	0.01	0.046

were in distilled water saturated with H_2S (it is not clear from the text whether the solution used for this particular set of experiments contained NaCl or not). The samples were notched cantilever beams. The author reported a 40% reduction of the threshold stress for SSC between standard and cold-worked samples, for materials of similar strength before cold-working (figure 4). Unfortunately, the degree of cold work and effect on hardness are not reported, and could not be estimated as the details of the cold-working procedure are left unclear. It should therefore be borne in mind that the data points for cold-worked material in figure 4 should probably be located further to the right, having higher yield stress values than the corresponding initial materials.

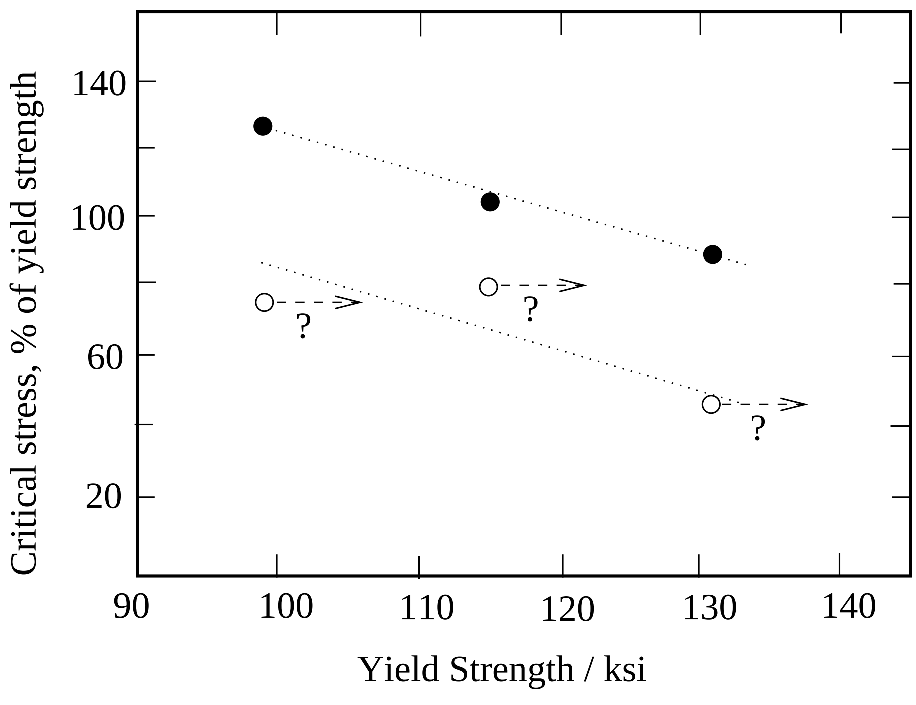

Figure 4: The effect of cold working on the critical stress for SSC in saturated H2S solution. After Dvoracek [14]. Filled circles are for unstrained material, empty circles for cold-worked. As in Dvoracek's work, the data for cold-worked material are shown assuming the yield stress has not been affected. This is, however, unlikely to be correct, as illustrated by the question marks indicating a possibly higher yield stress value.

Levesque [15] reported that the resistance to SSC was most affected by the first 1% of strain, but not significantly by further cold work up to 6% strain. Unfortunately, materials and many experimental details are not specified.

Joosten *et al* [5] have investigated the influence of cold work, yield strength and temperature on SSC of a quenched and tempered grade C-90 steel, the composition of which is shown in table 5. Tests were carried out in a solution of distilled water with 5% sodium chloride and 0.5% glacial

Table 5: Composition of the C90 steel used in Joosten *et al*'s investigation [5].

Elt	C	Mn	P	S	Si	Mo	V	Nb	Al	Ti
wt%	0.31	0.87	0.002	0.002	0.27	0.43	0.008	0.016	0.067	0.15

acetic acid. The solution was saturated with H_2S. Unstrained, 2.5% and 5% strained specimens (V-notched) were tested in three point bend at various loads so as to determine the threshold for cracking during a 100 h exposure. In all cases, the plastic deformation was induced by tensile straining of longitudinal sections of pipe. The reference yield stress was that of the as-received material throughout. The authors concluded that cold work had no detectable effect on the threshold stress level. However, this conclusion was not a direct observation, but was drawn from a statistical treatment of experimental results, in which five fitting parameters were inferred from fifteen data points. It is likely that there would be a large uncertainty on these parameters, and therefore on the conclusion drawn by the authors. This uncertainty was not quantified in the above reference. Of the fifteen experimental results presented by these authors, only two allow a direct assessment of the effect of cold work, and these indicate either a reduction or no effect on the threshold stress.

More recently, a number of studies have been concerned with the effect of cold expansion on the resistance to sulphide stress cracking of pipes [16, 17, 18, 19]. Mack *et al* [16] investigated the SSC resistance of L-80 (as-received yield stress 615 MPa) and P-110 (as-received yield stress 908 MPa) pipes before and after expansion by 10 and 20%. The tests consisted of four point bend samples loaded at 100% of their yield stress, in NACE solution A saturated with H_2S and in less severe conditions (5% NaCl in distilled water, 2.5% H_2S with balance CO_2). The results suggest an effect of straining in both materials. However, this is not perceived in L-80 when testing in the mild sour solution, as the material passed all the tests, or in P-110 in the 100% H_2S solution, as all the tests failed. The reference yield stress was that of the actual material and therefore accounted for possible effect of cold work. Interestingly, the P-110 grade showed a significant drop in longitudinal yield stress after expansion (from 908 in the as-received condition to 680 MPa for both 10 and 20% expanded). As the actual yield stress was used to determine loading conditions for SSC tests, the P-110 tubing material would have been tested at a significantly lower stress (680 MPa compared to 908 MPa) when in the cold expanded condition.

By contrast, the same authors only used the as-received yield stress for determination of loading conditions in further work carried out on P-110 material [18, 19]. In this case, tests were carried out using C-ring specimens in a solution of 5% NaCl in distilled water (gas: 1% H_2S/balance CO_2) and stressed to 100% of the as-received material yield stress. The composition of the materials investigated are given in table 6. As in the earlier study [16], cold work and strain ageing appeared to be significantly detrimental to the SSC resistance of the material. This works also shows that, not only can failure occur as a result of straining (in a material which would otherwise pass the given SSC test), but also that it tends to occur faster with increasing degree of plastic strain. These results are however reported qualitatively as graphs with an arbitrary scale and it is therefore not possible to exploit them further.

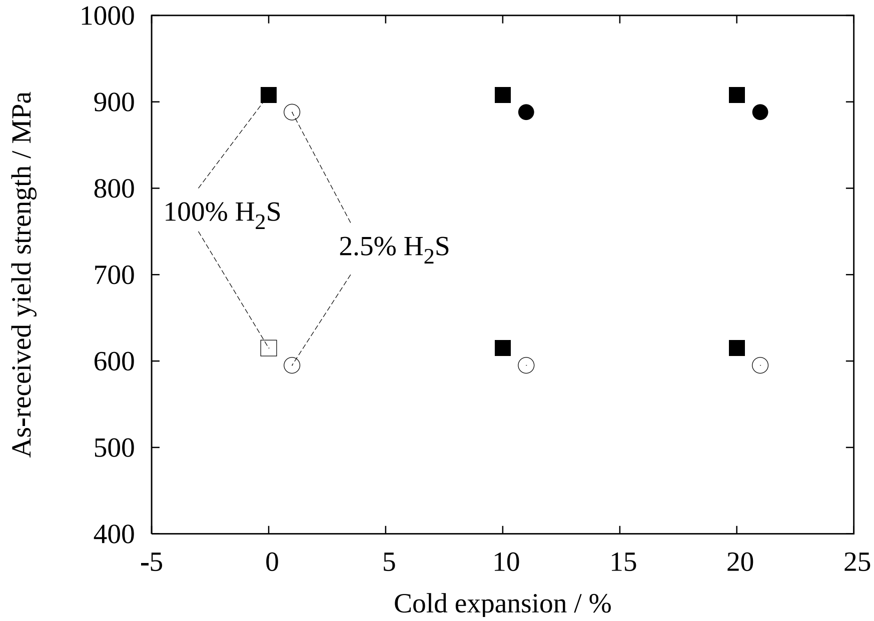

Figure 5: Outcome of SSC tests in 100% H_2S (squares) and 2.5% H_2S (circles) solutions, for L-80 and P-110 pipe materials, using data from [16]. Empty symbols indicate a pass, filled symbols a fail.

Table 6: Chemical compositions of the steels investigated by Mack *et al* and Sutter *et al*. All elements in wt%.

C	Mn Cr	P Mo	S V	Si Nb	Cu Al	Ni Ti	Authors YS(/MPa)
0.26	0.93 0.02	0.013 <0.01	0.003 0.048	0.26 -	0.02 0.048	0.02 -	Mack *et al* L-80 615 (636 expanded 20%)
0.25	1.36 0.25	0.007 0.19	0.009 ¡0.001	0.25 -	0.01 0.027	0.02 -	Mack *et al* P-110 908 (680 expanded 10 and 20%)
0.15	0.94 0.1	- 0.01	- -	0.21 -	0.07 -	0.04 -	Sutter *et al* [17] 292 (440 expanded 15%)

Sutter *et al* [17] carried out a similar investigation on a proprietary grade developed by Vallourec and Mannesman Tubes, using C-ring specimens in NACE solution A saturated with H_2S. All specimens survived, which unfortunately does not lead to any conclusion as to the effect of cold work on SSC resistance.

A detrimental effect of cold-work was also demonstrated by Shenton [20]. In this study, cross-weld four point bend samples were taken across a girth weld after different longitudinal straining programmes aimed at reproducing the strains developed during reeling of pipes. These were tested in NACE solution A saturated with H_2S for 720h. Again, while the hardness and yield stress of the material were only moderately affected by the cold work, there was a clear detrimental effect of deformation on the resistance to SSC.

Recent work carried out at TWI [21] on cross-weld samples has demonstrated that, for material having a hardness close to the recommended maximum of 250HV, a strain of approximately 1% was sufficient to cause failure at 90% of the parent material actual yield stress (YS 444 MPa). By contrast, 1% strain was not sufficient to cause failure at 90% of the parent material yield stress in a material of lower hardness.

These results strongly support the view that the impact of cold work on SSC resistance cannot be understood through work-hardening alone. In fact, Treseder and Swanson [13] had proposed, as early as 1968, that the traditional hardness criterion was not applicable to cold-rolled steels.

Discussion

There is a general agreement that the effect of cold work on SSC resistance is detrimental and progressive. This is clearly indicated by the results of Treseder and Swanson [13] or Mack et al [16]. While a number of studies report failures of cold-worked materials with otherwise acceptable hardness levels, there are not enough data in the literature to estimate quantitatively the impact of cold work on resistance to SSC at constant (cold-worked) hardness. In addition, very few studies have looked at the effect of small amounts of deformation (<5%). Work carried out at TWI so far confirmed the detrimental influence of even a small amount of plastic strain, however, in this instance, this is limited to material having a hardness close to the recommended maximum. In other words, it does appear that even small amounts of plastic strain should lead to a reconsideration of the common 250HV limit for sour service, or indeed whether any hardness criterion is applicable.

Except where mentioned, the results discussed in the literature are relevant to parent material rather than welds. There is no reason to question that such results would also apply to welds, and in fact, the effect of straining may be felt more severely because of the heterogenous properties across a weld and the presence of stress/strain concentration at the weld toe [22]. Results obtained at TWI have indicated that the strain distribution across the weld is highly concentrated near the weld root toes, sometime exceeding the uniform strain value by a factor 3 or more. This suggests that values of plastic strain thought to be safe for parent material may not be so when applied across a weld.

SSC MECHANISM AND ROLE OF COLD-WORK

The mechanism of SSC

It is now generally agreed that SSC, at least of non-nickel bearing low-alloy steels in severely sour environments, is only a manifestation of hydrogen embrittlement (for example, references [23] and [24]). Occurrences of cracking in low-alloy nickel steels, e.g. ASTM A203, [25, 26] have been linked with anodic dissolution rather than hydrogen embrittlement. In less severely sour environments, some authors have suggested that degradation during slow strain rate tests was dominated by conventional SCC (anodic dissolution) for annealed samples of AISI 1020, while hydrogen embrittlement was the main cause of degradation in cold-worked samples [27].

There is a number of questions that are of interest when considering the problem of SSC as a hydrogen embrittlement phenomenon: the effect of cold work on hydrogen uptake, whether a change in hydrogen uptakes translates into a change in SSC resistance, *etc.* It is perhaps worth repeating here that the present review is not concerned with the effect of plastic straining in a hydrogen charging environment, and therefore with issues such as the effect of dislocation movement on hydrogen entry, but rather with the effect of plastic strain on subsequent hydrogen embrittlement sensitivity. Even within these limitations, there is a much larger body of work on the effect of cold work on subsequent resistance to hydrogen embrittlement and the following does not claim to be an exhaustive review.

Cold work and hydrogen uptake

Bearing in mind that SSC in severely sour environments is a hydrogen embrittlement phenomenon, not only the effect of cold work on embrittlement, but also the effect of hydrogen uptake will be relevant.

The study of hydrogen in steels is often complicated by the fact that hydrogen is present in a variety of states. The lattice solubility of hydrogen depends on the hydrogen pressure, and follows:

$$x_H = 0.00185\sqrt{P}\exp -3400/T \tag{2}$$

where x_h is the atomic fraction of hydrogen in the lattice, P is the external hydrogen pressure and T the temperature. In standard conditions, it is extremely low (*ca* 2^{-8}) [28], and most of the hydrogen present in steels in these conditions is located at traps. Traps generally refer to lattice defects (vacancies, dislocations, grain boundaries) or microstructural features (*e.g.* second phase interfaces) to which the hydrogen binds more or less strongly. Binding enthalpies have been measured for a variety of cases and a detailed table can be found in reference [28]. Traps are usually categorised as strong and weak traps, or irreversible and reversible respectively. Hydrogen can escape from weak traps at room temperature. Nevertheless, these weak traps slow down the apparent diffusion of hydrogen considerably when compared to extrapolation of high temperature measurement of lattice diffusion, as illustrated in figure 6. Weakly trapped and lattice hydrogen form

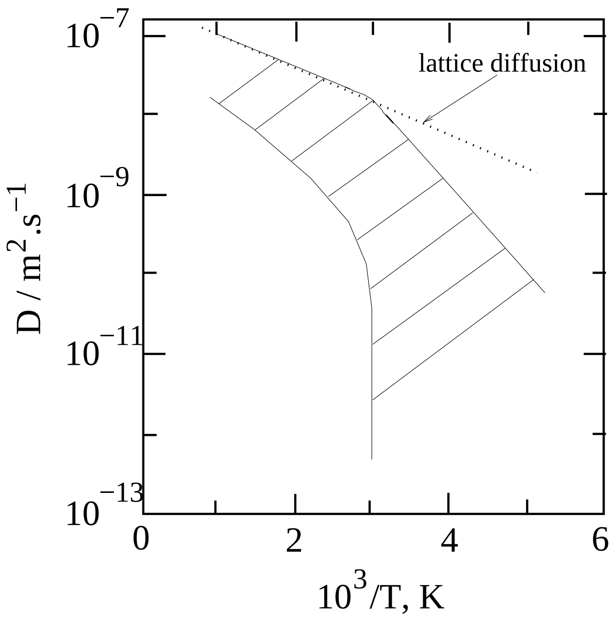

Figure 6: Range of diffusivity of hydrogen as a function of temperature, illustrating the role of reversible traps at low temperatures. After [28].

the diffusible hydrogen. Under normal conditions, the hydrogen lattice solubility is so low that most of the diffusible hydrogen corresponds to weakly trapped hydrogen. By contrast, strongly trapped hydrogen can only escape the material at higher temperatures (typically above 250 °C).

Cold work results in an increase in both vacancy and dislocation densities, and one would therefore expect the hydrogen content of a steel to increase with cold work. Numerous studies have indeed reported such effects. For example, Hudson and Stragand [29] measured the hydrogen concentration in steels cold-worked to different amounts, after different exposure times to an aqueous

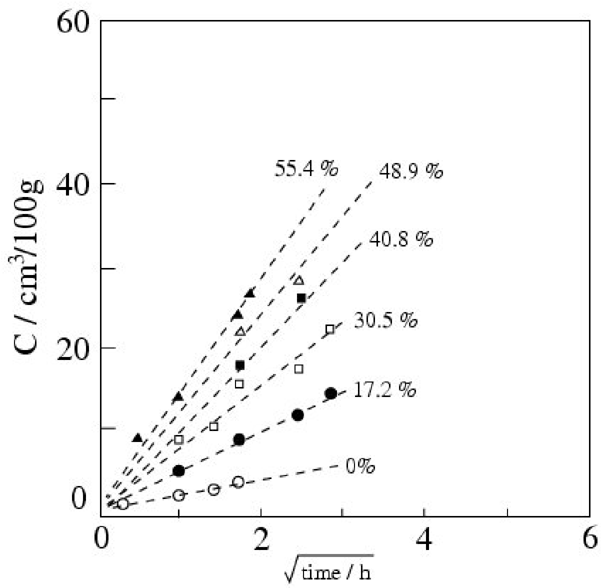

Figure 7: Hydrogen concentration as a function of exposure time to an aqueous H_2SO_4 solution. After Hudson and Stragand [29]. Cold work increases the amount of hydrogen absorbed and the rate of absorption.

H_2SO_4 solution. The results indicated that not only the total hydrogen concentration but also the rate of absorption increased significantly with increasing amounts of cold work (figure 7).

Huang and Shaw [30] have investigated the effect of cold work on the electrochemistry of corrosion in sour service and found that an increase in cold work leads to an increase in corrosion rate and potential. The current density increased for up to 20% cold work (thickness reduction). The authors suggest that this is due to surface alteration by the cold working process, which in turn enhances both ad- and absorption of hydrogen [4]. Huang et al [31] have later confirmed that cold work results in both an increase in permeability and a decrease in diffusivity of hydrogen in steel. This implies an increase in the 'solubility' of hydrogen in the steel (since permeability is a function of diffusion and solubility), and the authors have suggested that cold work enhances hydrogen uptake.

Recent work by Nagumo *et al* [32] has demonstrated an effect of both the Mn content and the temperature of straining on the resulting increase in hydrogen content (figure 8, left). Hydrogen absorption increased with plastic straining, and more importantly, increased as the straining temperature was decreased (figure 8, right).

Hydrogen content and embrittlement

There is no questioning, from the literature, that cold-worked materials will absorb more hydrogen and will do so faster than annealed materials. This leads to the question of whether embrittlement and hydrogen content are correlated. Numerous results indicate that this is the case. For example, Lucas and Robinson [33] have reported a strong correlation between threshold stress intensity and diffusible hydrogen content, as illustrated in figure 9.

Fuchigami *et al* [34] have made similar observations using the reduction of area in slow strain rate tests. Shim *et al* [35] have reported a continuous decrease in the notch tensile strength of 4340 steel after hydrogen charging for different lengths of time (leading to different hydrogen content). Luppo and Ovejero-Garcia have also reported a direct correlation between diffusible hydrogen content and embrittlement in an ASTM A516-G60 steel [36]. In this case however, the result is perhaps

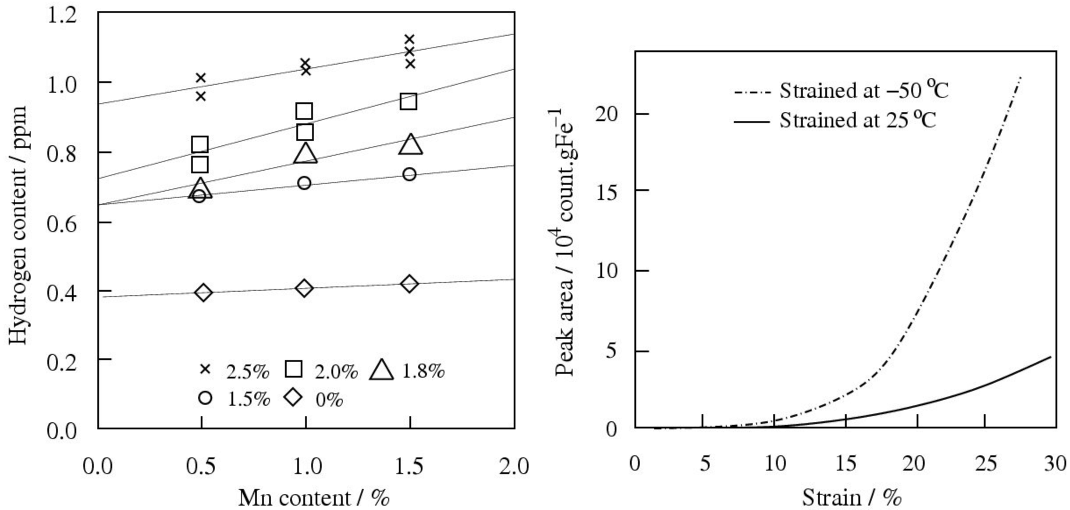

Figure 8: Left: effect of strain and manganese content on the amount of hydrogen absorbed in identical conditions. Right: effect of the temperature at which the material is strained, on the amount of hydrogen subsequently absorbed in identical conditions. After Nagumo *et al* [32]

overstated as the variations in hydrogen content relate to microstructural differences which may therefore also influence the results.

As stated earlier, the above does not claim to be an exhaustive review. It does not appear to be contested, however, that there is a direct link between diffusible hydrogen content and degree of embrittlement. Nevertheless, it has been underlined that hydrogen was present in a variety of states (in solution, trapped at interfaces, *etc*), and the question therefore arises whether all contribute equally to the embrittlement phenomenon.

The distinction between weak and strong traps has been introduced earlier. It is well established that strongly trapped hydrogen does not participate in the embrittlement phenomenon [37, 38, 39] and in fact, there have been attempts to exploit this to design steels that would be more resistant to hydrogen embrittlement [40]. That embrittlement is the result of weakly trapped hydrogen has been demonstrated in a number of studies, such as that published by Takai *et al* [37]. The latter reports no embrittlement effect for as high as 2.9 mass ppm hydrogen strongly trapped (binding energy $\sim$ 65 kJ/mol), but a strong embrittlement effect with 0.8 mass ppm weakly trapped hydrogen (binding energy 25 kJ/mol). The authors suggest that weak traps could include vacancies, dislocations, grain boundaries and ferrite/cementite interfaces.

Recent work by Nagumo *et al* [39, 41], Nagumo [38] and Fuchigami *et al* [34] have underlined the role of vacancies in the hygrogen embrittlement of plastically deformed steels. A number of similar experiments were carried out on steels of different compositions, in which the hydrogen absorption was measured after straining to 2 or 5% plastic strain. When a 1h annealing was carried out at 250 °C after straining but prior to hydrogen charging, the hydrogen absorption was identical to that of the unstrained material. As this temperature is not sufficient to allow dislocation annihilation, it was concluded that vacancies were responsible for most of the increase in hydrogen absorption.

Concluding remarks and applicability to SSC resistance

Work carried out on the effect of cold work on hydrogen embrittlement consistently indicates a detrimental effect. Straining accelerates the hydrogen uptake and increases the maximum amount that can be absorbed. The embrittlement of samples charged with hydrogen is worse following

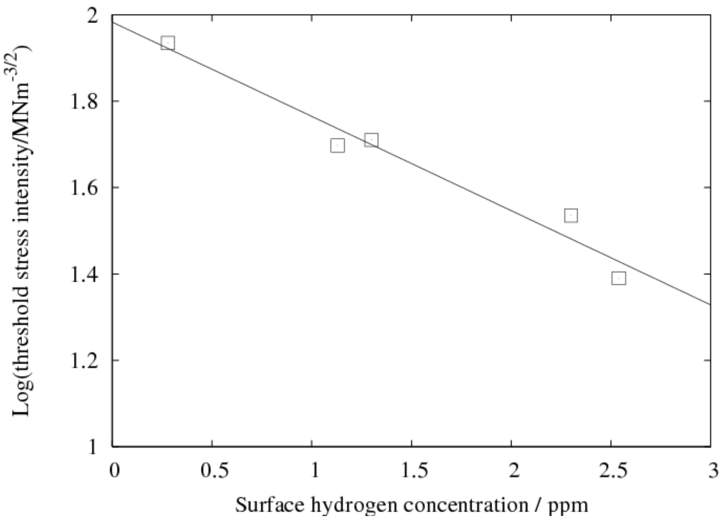

Figure 9: The influence of hydrogen content on the threshold stress intensity for steel BS4360 Gr50D, with a hardness of 405 HV (±25). After [33].

straining, and there is good evidence that this is essentially the result of vacancy generation during straining.

However, it is difficult to infer, from this viewpoint, whether this should apply to sulfide stress cracking. Hydrogen embrittlement problems broadly fall in two categories. In the first one, hydrogen is present in a given quantity, after welding for example. In the second, there is a continuous entry of hydrogen, as is the case during exposure to sour environments. The role of hydrogen trapping is clear in the first case: embrittlement is mostly dictated by how much of the weakly trapped hydrogen is able to diffuse to a crack tip, that is, how much diffusible hydrogen is present in the steel.

In the second case, because there is continuous supply of hydrogen, it is not clear whether increasing the concentration of weak traps would be of consequence. Much speculation could be carried out on this topic, which is out of the scope of this review. It is worth pointing out that TWI is currently carrying out an investigation of the problem. In this program, cross-weld samples will be strained to 1% plastic strain at room temperature or at -50°C. Four point bend tests will be carried out in NACE solution A, at a stress level known to be close to the threshold for the selected material after 1% straining at room temperature.

SUMMARY AND CONCLUSIONS

Very few studies were found that dealt with the effect of small amounts of cold work on the performance of C-Mn steel welds in sour service. In addition, results are not easily comparable because of variations in experimental method and parameters.

There is a general agreement that plastic strain affects the resistance to sulphide stress cracking, even possibly for low amounts of strain and without significant changes in hardness.

However, available data remains scarce, in particular, few studies if any have published sufficient details for a full examination of the mechanisms at work. As an example, the degree of work-hardening is often not investigated, and render difficult the isolation of any effect on the SSC resistance that would not be related to an increase in yield stress. Also, results such as those shown in figure 1 possibly illustrate an effect of the microstructure, as a normalised steel seems to be affected more severely by strain than a quenched and tempered material. It is clear that quantifying the effect of strain on SSC resistance will require a detailed study involving not only SSC tests, but also a caracterisation of the changes in mechanical properties and in hydrogen absorption capacity for strained materials.

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