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Failures due to hydrogen embrittlement

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ABSTRACT

The effect of hydrogen in metals and alloys are discussed. The various trapping and cracking processes by which hydrogen affects the behaviour of materials are summarized. Hydrogen may be introduced during melting and entrapped during solidification or it may be picked up during heat treatment, electroplating, acid pickling ,or welding. Hydrogen also can be introduced by cathodic reaction during corrosion. Embrittlement mechanisms have been described by highlighting the models such as: (i) planar pressure, (ii) cohesive energy, (iii) surface energy, (iv) dislocation, (v) hydride formation and (vi) methanation. Unlike most embrittlement phenomena, hydrogen embrittlement is enhanced by slow strain rates. The strain rate sensitivity, temperature dependence and susceptibility to delayed fracture are main characteristics of hydrogen embrittlment. Two case studies of failure analysis of high C steel wire products are presented. The tools and techniques for such analysis have been pointed out. It has been shown that planar pressure model and cohesive energy model can explain well the failures observed in those two cases.

INTRODUCTION

The effect of hydrogen (H) has been a subject of extensive studies to understand the mechanisms for degradation in mechanical properties of metals and alloys [1,2] since the industries often encounter the failure of products due to hydrogen embrittlement (HE). H, after entering inside the lattice, reduces the ductility and leads to delayed fracture under stressed condition [1]. In the present paper we will summarize the effect of H in metals and two case studies which are related to HE – one due to molecular hydrogen and other one due to atomic hydrogen. In one case H has been picked up from melting practices and in the other case it has been possibly picked up from improper pickling operation, while processing high C steel (eutectoid steel) for cold drawing operation.

Trapping and Cracking Mode

Fig. 1 summarizes the overall scheme of H source, transport paths, destinations and fracture mechanisms [3a]. H can enter the metal in a number of ways. During melting practices, H remains dissolved in liquid metal and subsequently in solid metal if vacuum degassing practices are not adopted properly. High amount H can exist either in (i) molecular form or (ii) atomic form or both. Initially H is absorbed in the atomic form in the lattice and then it diffuses to grain boundaries, dislocation cores, interfaces of coherent and incoherent precipitate, inclusions, voids etc. Generally, atomic H transforms to molecular H in the case of higher concentration of H. Molecular H stays in the voids or pores or interfaces. If these defects are not present in the vicinity of high H concentrated area, then flakes or hair line cracks are formed to release the high pressure. In equilibrium situation, both atomic and

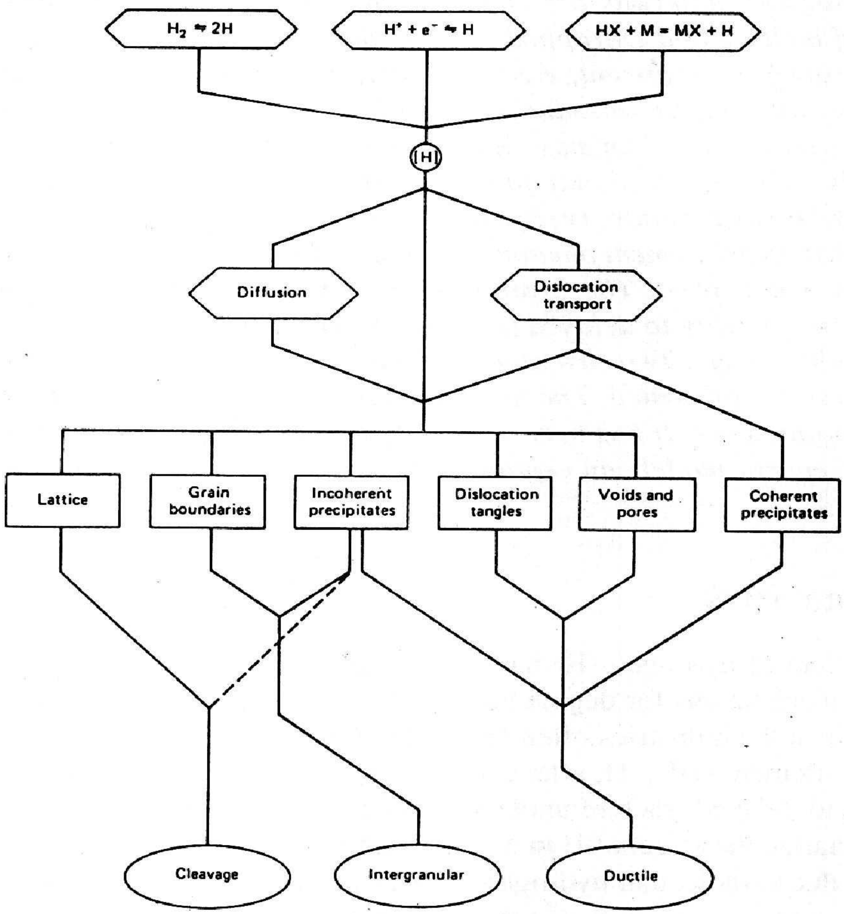

Fig. 1 : Flow diagram depicting hydrogen sources, transport paths, destinations, and induced fracture micromechanisms [3a]

molecular H will be present inside the material at higher concentration of H. Highly tensile stressed region will be the suitable place for atomic H. During welding, H picked up from residual H_2O or electrode, diffuses to base plate when weld is hot and causes problem while cooling weld heat affected zone. This is known as cold cracking. During electroplating and pickling, H can enter the lattice, which should be avoided by subsequent baking treatment (200-250°C).

It is now accepted that molecular H is dissociated by chemisorption on the surface of metals allowing liberated atomic H to enter and embrittle the metal. Similarly, it has also been shown that H is a product of corrosion reaction between Fe and H_2O; this liberated H can enter metal the same way as chemisorbed H. Thus it has been argued that stress corrosion cracking (SCC) resembles HE in certain cases. Fig. 1 shows that absorbed H can be transported by diffusion or dislocation movement. It has been found that transport through dislocation is several orders of magnitude greater than through lattice diffusion. Generally H has a tendency to get trapped in defect sites of materials. Finally, it can be seen that cracking process can lead to one of the micro-mechanisms such as : (i) cleavage, (ii) intergranular, or (iii) ductile (microvoid coalescence) fracture. All the three mechanisms in the same steel alloy when tested at different stress levels, have been reported in literature [3b]. Therefore, depending on materials and parameters the characteristic fracture surface of HE can be generated.

Embrittlement Mechanisms

There are several theories that explain HE. However, the most important models will be highlighted. One of the model [4], called, "Planar pressure mechanism" predicts that high pressure developed due to H with gas pores inside the material causes the cracking. Although this model explains the embrittlement of high H charged metal, this model cannot be accepted as universal model for HE as it can not explain delayed cracking phenomena. Second model proposed by Troiano and Coworkers [5], suggested the reduction of cohesive strength due to presence of H atom. Actually H atom diffuses easily to a region of high tensile triaxiality present at the tip of the crack and assisted crack propagation by reducing the cohesive strength. Thus crack propagates intermittently depending on the critical concentration of H atom to be built up near the tip of the crack. A third model [6] based on the reduction of surface energy, leads to easy crack growth in the presence of H. A fourth model proposed by Beachem [7] and discussed by others is based on enhancement of dislocation mobility which induces highly localised plastic flow at very low stress levels. Finally HE is also explained by metal hydride formation [8] in materials such as (group IVa & Vb) as titanium, vanadium and zirconium. It has also been suggested that hydride induced embrittlement may also occur in steel containing those metals. A completely different type of HE in presence of H and C in plain C-steel at high temperature and pressure occurs due to formation of methane inside the material. The formation of methane due to development of high pressure causes blistering and failure observed in petroleum industry [9]. This process produces decarburization and is somewhat different from low temeperature HE.

FAILURE ANALYSIS OF COLD DRAWN WIRE OF HIGH C-STEEL

The continuous cast billet of 11x11 cm was hot rolled to produce wire rod, which were showing bulging problem, due to hydrogen [10]. After increasing soaking time and temperature the bulging problem disappeared but sliver problem appeared during cold drawing operation.

Cold drawn wire exhibited the formation of chips (similar to seams) and also led to failure during wire drawing operation. The samples near the surface imperfection and the fractured surface were investigated. The present problem deals with study of the surface imperfection and failure of cold drawn wire [11].

Experimental Details

Wire of 3 mm diameter was cut to make the transverse and longitudinal sections for metallographic and hardness measurement. Diamond paste was used to polish the sample in order to avoid the contamination from alumina particles. The samples were analyzed before and after etching. The fractured surface and rolled surface containing the chips or seams were investigated under Scanning Electron Microscope (SEM). The hardness test was also performed on the polished surface of longitudinal and transverse sections of the samples.

Results

The polished and unetched sections under optical microscope shows the presence of pores or holes (Fig 2a). The abundance of the pores in many places is recorded as high as 6% from quantitative image analysis and minimum 2% through out the sample. The size of the holes is estimated to be of various sizes with a maximum range of 20μm and of nearly spherical shape. Pores and indusions are distinguished by changing focussing condition. Fig. 2b shows the pores are bright but not the inclusions in overfocussed condition. The coalescence of pores has led to the formation of cracks aligning along the rolling/drawing direction. The inclusions of calcium and potassium aluminosilicate were also identified. In some cases, the inclusions are also found to be lying within the pores which makes the quantitative analysis of pores alone difficult. However, from the various reading, it can be mentioned that pores and inclusions both are present but the pores are more than the inclusions (Fig. 2).

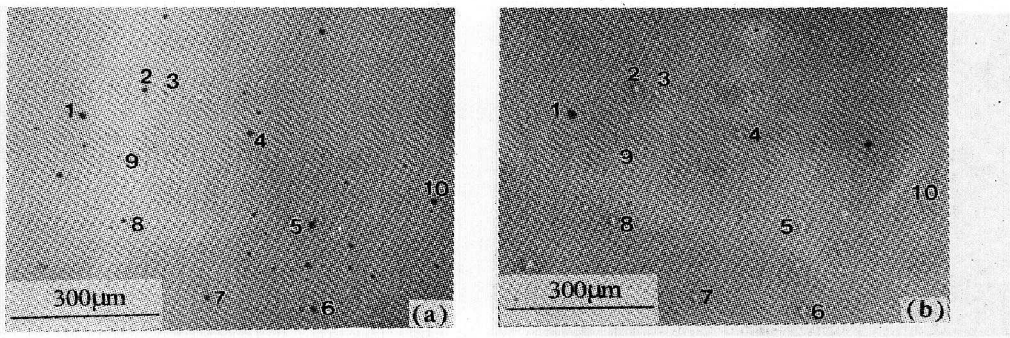

Fig. 2 : Optical micrograph of unetched wire drawn sample, (a) transverse section shows abundance of pores in focussed condition, (b) overfocussed condtion showing pores as illuminated spots and inclusions as dark spots. The correspondence between (a) and (b) can be noted.

Surface of the wire containing seams and chips were investigated under SEM. Fig. 3 shows. the surface cracks containing inclusions. The inclusions by EDX analysis confirmed the same type as mentioned earlier. The inclusions can also be identified near the chips.

Fractured surfaces of the wire which failed during drawing operation can be observed in (Fig. 4). Inclusions are located in the interface of fibrous and radial zones of the fractured surface. However, the presence of the inclusions are not significant in the fibrous zone. In addition to the above features, the preexisting and unwelded pores can be found from detailed analysis of the fractograph, which has led to dimpled fracture typical of ductile fracture.

The etched surface near the chips was observed under optical and SEM. The fine pearlitic microstructure on the transverse section has been noticed (Fig. 5a).

Fig. 3 : SEM of surface cracks showing the presence of mostly calcium alumino-silicate type of inclusions.

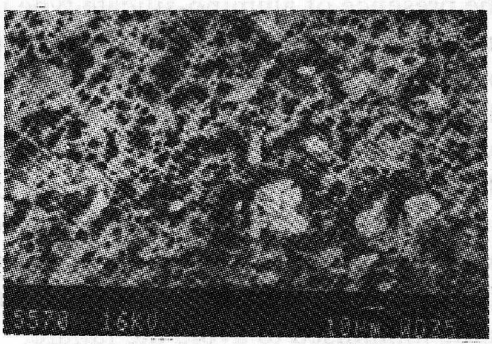

Fig. 4 : SEM fractograph of wire failed during operation, exhibiting dimples and indicating ductile fracture. Inclusions can also be observed.

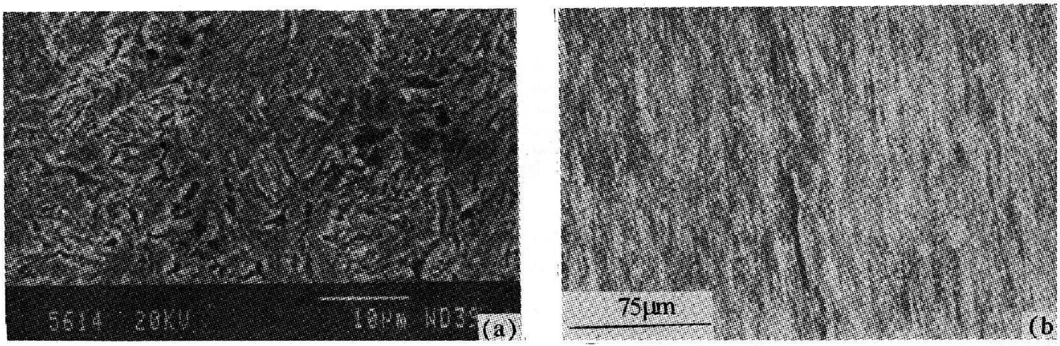

Fig. 5 : (a) SEM photograph of transverse section shwoing pearlitic microstructure; (b) optical micrograph of longitudinal section depicting the presence of perlitic microstructure and cracks along the drawing direction

Elongated pearlitic structure and cracks along the drawing direction has been observed in the longitudinal specimen (Fig. 5b). The hardness data of the sample has been found around 400 VPN which indicates the high degree of cold working of the material.

Discussion

The pores or holes which are found to be abnormally high in the present sample must have originated during solidification of continuous cast billet because of improper degassing. The pores or holes are generally segregated near the central line of the ingot. During later stages of hot working, pores segregated in a localised region may coalescence and lead to the formation of the cracks. Subsequently when these hot rolled wire rods are further reduced in diameter (say, below 5mm) by cold drawing the presence of the cracks and holes may create problem leading to imperfections and even failure of the wire. The situation is more vulnerable in the presence of alumino-silicate type inclusions which are observed in the present investigation enhances the rate of failure because of their non-plastic nature. The pores may be due to the gas evolution (possibly hydrogen in the present case) during solidification. If proper degassing treatment is not maintained, the gas content will obviously lead to the problem. During soaking treatment, the gas entrapped in the holes gets a chance to diffuse out of the holes and the empty hole may subsequently get welded during hot rolling. The present investigation obviously points out to either improper degassing treatment or insufficient soaking treatment. The control of calcium-alumino-silicate inclusions as they are non-plastic requires to be minimised to avoid the failure.

Conclusions/Recommendations

1. High amount of hydrogen content along with alumino-silicate type non-plastic

inclusions seem to be responsible for the present failure.

2. Insufficient soaking treatment and improper control of degassing practice appears to be main cause for the abundance of the pores. More soaking time may reduce the problem. The optimum solution between the degassing and soaking treatment can be found out after some more detailed investigation.
3. The content of the alumino-silicate particles should be brought down to reduce failure rate. The role of non-plastic inclusions during drawing operation is always harmful to enhance the failure rate. The optimum level of inclusions along with the pores needs to be established to avoid the problem.
4. Cooling rate during continuous casting is an important factor, which may be so high in the present case that it does not allow the gasses to go out of the billet. Therefore, some control, if possible to exercise, may reduce the occurrence of failure.
5. More investigation in this direction to optimise the process parameters (i.e., slag practice, degassing, cooling rate, soaking treatment etc.) are strongly recommended to eliminate the problems of slivers, seams and any other surface imperfections generated during rolling and drawing operations.

FAILURE ANALYSIS OF HOT DIP GALVANIZED HIGH TENSILE WIRES[12]

Wire rods of 12 mmø with a nominal composition of C-0.82, Mn-0.7, Si-0.2, S-0.02 max. and P-0.02 max. are first pickled and baked at 150°C for 15 minutes, followed by coating. Wires are pre-drawn to 100 mm dia. before patenting. A gap of 10 hrs. is allowed between coating, pre-drawing and patenting. Subsequent to the patenting, the pickled wires are dipped in hot water and drawn through the flux to 6mm size. This is followed by galvanizing and final drawing to 4.15 mm ø. The failures are reported at this stage in addition to the failures during spooling and stranding.

Several types of wire rod failures are reported in literature some of which are bulging, flaking splitting etc. There are no reported cases of failure by strain ageing in high carbon cold drawn steel wire rods.

Splitting failures may occur spontaneously when the material is embrittled along a longitudinal plane or when the residual stresses generated during the drawing and handling operations are relaxed through splitting. Cold drawn high carbon steel wires are amenable to being more weak along longitudinal planes rather than transverse planes due to the fibre-like deformation of pearlitic phases in the longitudinal directions [12]. It is also possible that further metallurgical embrittlement may take place due to interfacial segregation, hydrogen activity etc. which makes delamination/decohesion easier [14]. The present investigation was carried out to confirm embrittlement, either due to metallurgical reasons or due to the presenc of hydrogen.

Visual Observations

The wire rods, which have failed at various stages, typically show a split alon the rolling direction. The longitudinal splitting into layers, during rolling operatior termed as delamination, is one of the qualitative indication of decrease in ductility No other distinctive features were observed on the wire rods.

Metallography

The wire rod samples were polished, with diamond paste in the final stage, an were examined under optical microscope. Typical features, from representativ areas, are shown in Fig. 6. In addition to the few inclusions that are observed, number of pores were present in most of the areas that were examined. It may b noted that the inclusions and the pores could be distinguished, from each other, by varying the focusing plane, as their planes of foci are different which has alread be demonstrated in Fig. 2(a,b). It is also observed that some of the pores hav coalesced to form a crack like defect.

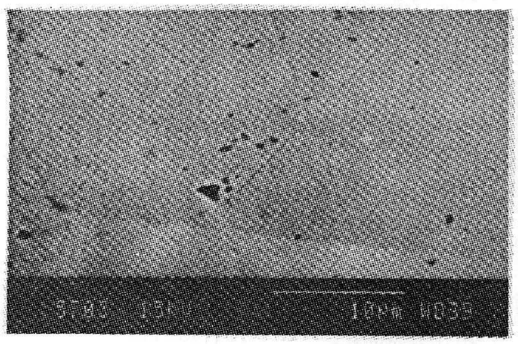

Fig. 6 : SEM photograph of unetched wire sample exhibiting pores and inclusions

Microstructure

Some of the polished and etched samples were examined under scanning electror microscope (SEM). Fig. 7 presents the typical features that are expected in a colc drawn steel wire rod, viz. fibrous appearance comprising of elongated ferrite anc cermentite lamella (pearlite).

Fractography

The longitudinal fracture surfaces of the failed surfaces, examined under SEM showed, again, fibrous appearance with secondary cracks (Fig. 8). A look at a

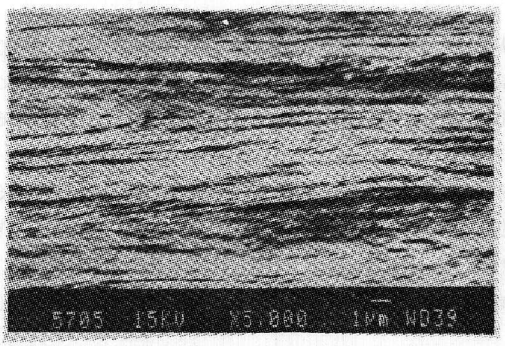

Fig. 7 : Microstructure featuring typical fibrous nature comprising elongated ferrite and cementile lamella (pearlite)

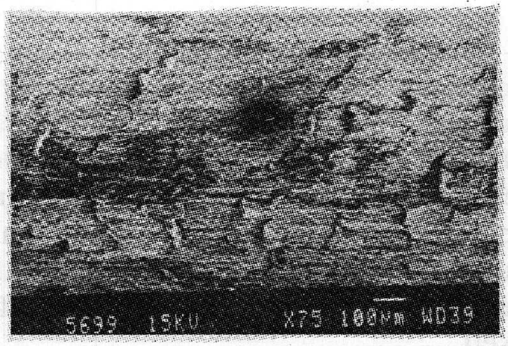

Fig. 8 : Subsurface secondary cracks, observed in splitted surface of failed wire, indicative of hydrogn damage

crack embedded in the material supports the failure to be termed as delamination. Comparing with the microstructural features (Fig. 7), it appears that the delamination has taken place either along the prior austenite grain boundaries i.e. along the interface of the pearlite colonies. The presence of some non-inclusion hard particles segregated randomly on the fracture surface are observed. EDX survey carried out on these tiny particles indicated them to be cementite. The formation of globular cementite during drawing occurs by the densification of cemented through wrinkling or buckling, and also by carbon diffusion accelerated due to deformation [15,16].

Mechanical Tests

As discussed in the introduction, hydrogen or some other mechanism has to be operative to produce abrupt fractures originating at hard particle interfaces, voids, pores etc. The presence of secondary cracks suggests hydrogen attack of some form or the other. Since there is no one single theory to prove hydrogen attack conclusively, recourse is taken, to confirm or eliminate presence of hydrogen in the steel wire rod samples, by conducting a few mechanical tests [17].

It is believed that a material affected with atomic hydrogen would show similar toughness value as that of the same material without any hydrogen in it, when tested under high strain rate (such as in the impact test) and that under slow strain rate test (such as in standard tensile test) would show significant difference in their toughness behaviour. Accordingly, few samples of 55 mm length were baked at about 250°C for 30 minutes, to eliminate any atomic hydrogen in the material, and tested in an impact testing machine along with a few as-received samples. The impact toughness results are shown in Table 1. It may be noted that although the specimen sizes were not of the same size as of the standard CVN toughness specimen, the values would serve the purpose of comparing one with another of similar dimensions. Both the lots showed an average value of 33J under identical test conditions.

The tensile specimens, with about 100 mm parallel length between the grip holders, were cut from the supplied wires and were tested on a servohydraulic machine. The nature of the Load-Displacement plots does not show any evidence of strain aging. Table 2 shows the tensile properties of the baked as well as the as-received samples. A dramatic change may be noted in the % elongation of the specimens, suggesting hydrogen embrittlement in the as received wire. A quantitative estimate of the residual hydrogen in the wires could not be attempted because such atomic hydrogen would diffuse during the specimen preparation stage itself.

A few delayed cracking tests were conducted on partially split wire samples, by hanging a dead weight to one of the split ends. The acoustic emission, collected from the specimen under stress. The signals generated were within 35-65dB range. It appears that the activity is of two types: one with lesser number of hits and the other with higher number of hits per event. This probably owing to the microvoids or decohesion generating less vigorous signal, and after a delay (approx. 5 hours), a more vigorous signal (higher number of hits per event) is generated when the micro voids coalesce to the preexisting crack by extending further or decohesion of crack is higher than the previous one due to higher concentration of H a head of crack tip.

It is a well known fact that hydrogen diffuses more readily, than any other gas at room temperature. The hydrogen, thus, diffuses into the material (crack tip) causing an abrupt failure of the wires. After the hydrogen has initiated the failure by a tensile residual stress at the axis of the wire, to splitting type of failures. During coiling or twisting, a plastic bending is induced in a plane which along with residual stress present causes the wire to fail by splitting along the weakest plane i.e. the direction of rolling [15].

Table 1 : Impact toughness test data

Condition	Test-1	Test-2	Test-3	Average toughness, (Joules)
As-received	34	36	31	33.7
Baked	33	35	32	33.3

*Table 2 : Tensile test results**

Specimen	% El.	σ_y, MPa	σ_u, MPa
As-received	3.02	1433	2204
Baked	5.32	1543	2178

*Values reported are average of three specimens

Concluding Remarks

Based on the investigations carried out, and the observations thereupon, it appears that the cohesive strength of the boundaries/interfaces was reduced by the presence of atomic hydrogen which ultimately leads to sharp splitting because of the presence of high tensile residual stresses in the central region of the wires developed during the drawing operation.

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