FRACTURE PREVENTION IN ENERGY AND TRANSPORT SYSTEMS

HYDROGEN INDUCED SURFACE EFFECTS ON THE MECHANICAL PROPERTIES OF TYPE 304 STAINLESS STEEL

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The possibilities of modifying the mechanical properties of type 304 stainless steel by cathodic hydrogen charging were studied. The situations analysed included hydrogen embrittlement itself in tensile tests of hydrogen containing samples and the effects of delayed cracks in fatigue tests of hydrogenated and outgassed samples. SEM and TEM observations were also performed. It was found that hydrogen induced surface delayed cracks appear in great quantity during outgassing (of the order of several millions in a square centimeter). Hydrogen embrittlement was responsible for drastic losses in ductility in tension, while surface cracks severely reduced fatigue life.

INTRODUCTION

Austenitic stainless steels have been commonly used as the appropriate material for hydrogen (H) production, storage and transportation components and also in several nuclear applications. This has stimulated a number of studies on the behavior of these materials in the presence of H rich environments. The early pioneering work of Blanchand et al (1) and Whiteman and Troiano (2) identified the effects of hydrogen embrittlement (HE) in austenitic stainless steels, which were considered unaffected by this problem up to then. They concluded that these steels may suffer HE, but the amount of hydrogen necessary to produce this phenomenon is one or two orders of magnitude greater than for b.c.c. materials. Following this, other studies (Holzworth and Louthan (3) and Nabashi and Galland (4) showed, by using either cathodic or gaseous charging, that hydrogenated austenite may present: i) phase transformations to ε and/or α' martensites; ii) surface delayed cracks and iii) loss of ductility in tension. These effects are particularly important for unstable austenitic steels, e.g., those with higher tendency for martensitic transformations.

Hydrogen induced surface modifications of electrolytic charged type AISI 304 stainless steel was characterized metallographically in a previous work (Evangelista and Miranda (5)). Based on this, the objective of the present paper was to identify the possibilities of altering the mechanical properties

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of cathodically hydrogen charged 304 stainless steel under two different aspects. One is related to the effect of H itself as contained in the sample and the other to the influence of the modifications left by H on the surface of outgassed specimens.

EXPERIMENTAL PROCEDURES

This study was carried out using two different types of AISI 304 stainless steels. One was a wire with 1.2 mm diameter and the other was a 0.6 mm thickness sheet. The wire's chemical composition in weight percent is C:0.059; Cr: 17.8; Ni: 7.9; Mn: 2.0; Si: 0.50; P: 0.022; Mo: 0.38; Fe: balance and that of the sheet is C: 0.050; Cr: 18.0; Ni: 8.5; Mn: 1.32; Si: 0.47; Mo: 0.11; S: 0.001; Cu:0.040; Co: 0.15; Fe: balance. Wire specimens were heat treated at 900°C for 10 minutes, yielding an average grain size of 20μm. Reduced diameter specimens (0.6 mm) were obtained by electrolytic polishing. Sheet samples with as received thickness were annealed at 968°C for 40 minutes and had a grain size of 25 μm. Thinner sheets were obtained by repeating twice the procedure of cold rolling at room temperature (RT) and annealing at 1065°C for 45 minutes, followed by pickling and electrolytic polishing. This yielded a grain size of 47 μm and a thickness of 0.15 mm. H charging was performed cathodically at RT in an electrolyte of 1N H_2SO_4 plus 100 ml (unless otherwise stated) of a 1g/l As_2O_3 solution, used as a $H^{\cdot}$ recombination poison. Tensile tests were conducted at RT in an Instron machine, model 1125, 10 minutes after charging. The gage length of wire specimens was 40 mm and that of flat sheet samples was 8 mm with a cross section of 5 x 0.15 mm. Fatigue tests were carried out in an MTS servohydraulic machine operating in the load control mode. Tension-tension conditions were used with a mean stress of 329 MPa. The flat sheet hour-glass specimens with 20 mm minimum gage width and a thickness of 0.6 mm were charged for 16 hours at RT at a current density of 1000 A/m^2. After that they were aged for 8 hours at RT and for 18 hours at 90°C, and then tested. SEM and TEM micrographs were also obtained. TEM samples were first thinned and then charged with H.

RESULTS

The characteristics of the delayed crack phenomenon produced by H charging on the surface of austenitic stainless steel depend strongly on the charging conditions. Figure 1 shows the variation of the number of cracks per unit surface area as a function of current density for two hours of charging, as well as the behaviour for both various times and percentages of the As_2O_3 solution at 1000 and 4000 A/m^2. It also presents typical SEM micrographs for three current densities for a time of 2 hours. These clearly show the increase in crack density with current density. The delayed cracks appear in groups within a grain aproximately parallel among each other and on twin and grain boundaries. Some of them are wavy while others are straight. These last ones are always present in regions where profuse ε martensite transformation has occured. This may be noticed on the left half of the unetched micrograph of figure 1.b and in more detail in fig. 2, which shows cracks on ε martensite within a twin. The cracks aproximately bisect the largest angle between ε platelets.TEM micrographs showing ε phase and cracks are presented in figure 3 and 4. The former shows ε phase in early stages of formation, consisting of single and overlapping stacking faults. In the latter two variants of ε martensite can be observed as well as a crack parallel to one of them. The lower edge of the crack runs along an ε band. All the cracks initiating in the edge of the samples (thinner regions) presented that feature. In the thicker regions cracks were also found in directions transversal to the ε bands, resembling those shown in figure 2.

Marked HE was obtained in tensile tests of wires and thin sheets of 304 stainless steel as can be seen in figures 5 and 6. The wire with reduced diameter and the thin sheet were more susceptible to HE showing considerable loss in ductility. Fracture and lateral surface cracks morphologies are detailed in figures 7 to 10. A "mud-like" crack pattern is produced by decohesion along grain and twin boundaries, as well as at cracks within the grains, due to the combined action of the applied stress and that of the hydrogen induced surface stressing on outgassing. The thicker specimens still show an over all ductile fracture (figures 7 and 9). The fracture morphology of figure 9 shows a dimpled ductile core region surrounded by a layer of fragile fracture, in which there are some areas of perfectly intergranular fracture and others with partly transgranular cleavage characteristic. Figure 10 shows the lateral view corresponding to the right hand side of figure 9. Analysis of both give a good idea of the depth of penetration of the surface cracks in this case. Figure 11 shows the results of the fatigue tests in annealed and hydrogenated specimens with an insert indicating a typical SEM observation taken at an inclined angle to the fracture surface. The presence of H induced delayed cracks on the surface of the specimen were effective in reducing the fatigue life.

DISCUSSION

It had been traditional in the past to consider the austenitic steels immune to the deleterious effects of H, specially if compared to the well documented problems observed in carbon and high strength steels. The reason for that is illustrated in figure 7, which is an example of a specimen severely damaged superficially but keeping a typical cup and cone ductile fracture mode. This happens because of the limited capacity of H to penetrate into the austenitic structure. The diffusion coefficient of this element in austenite at RT is in the range of $2.3 - 8.0 \times 10^{-16}$ m^2/s (Atrens et al (6) and Narita et al (7), while in ferrite it is of the order of 1.5×10^{-9} m^2/s (Fast (8)). A rough calculation based on this data shows that in a 24 hr period at RT the depth of penetration of H in austenite would be about 20 μm while in ferrite it would penetrate over 10,000 μm. In a hydrogenated stainless steel (figure 7) this leads to a situation in which a "composite" specimen is obtained, made out of a ductile core surrounded by a thin fragile layer. The mechanical behaviour of this outer layer will depend on a compromise between the contributions of different phenomena. The presence of H in austenite may induce the weakening of atomic bonds, a decrease in the stacking fault energy (SFE) and severe compressive stresses (4), (Fujita (9)) due to the accumulation of large amounts of H in a thin layer enhanced by the combined effects of a high solubility and a low diffusivity. In the presence of compressive stresses the way austenite finds to partially relax them is to transform into the hcp ε phase. This process is favored by the lowering in SFE and is accomplished during hydrogenation. It has also been suggested that there may be hydride formation during hydrogenation, which still remains as a controversial fact (Mathias et al (10)). When charging is over the material begins to outgass, generating surface tensile stresses which, helped by the weakening of atomic bonds, give rise to delayed cracks. Also there is a partial transformation of ε into α' martensite as well as back into austenite. This discussion is partly referred to by different authors (3,4,7,10) and is presented in schematic form in figure 12. It is important to emphasize that the martensitic phases (ε and α') induced in unstable austenite by H are the same ones which occur as a result of cold deformation of this material (3,7). They are crystallographically identical.

Two kinds of effects on the mechanical properties of unstable austenitic stainless steels can be expected from the process described above. One of them

is due to the presence of H itself and the other takes into account the defects remaining in the outer layer when H has escaped. The former could be considered as the actual HE and was analysed in this work through uniaxial tensile tests. The results herein presented in figures 5 to 10 emphasize the HE in tensile tests. The mechanical properties depend on the geometry of the sample. Higher values of surface to volume ratio increases the sensibility to HE. This can be firstly noted in figures 5 and 6 which show larger loss in ductility for the thinner wire and drastic fragility for thin sheet specimens. A typical fracture morphology for non severe charging of the thin sheet (figure 9) shows an outer region of brittle fracture surrounding a core of a ductile dimpled structure. This core has the typical appearance of the well known (Hänninen and Hakarainen (11) ductile fracture morphology of type AISI 304 stainless steel. Extensive surface cracking appears in figures 8 and 10, even though they correspond to samples with some ductility. If the depth of penetration of H into these samples would have been of a magnitude comparable to their diameter or thickness, the surface cracks would then have played a major role contributing to a mostly fragile fracture. The effect of HE in austenitic stainless steel predominates in tests conducted shortly after hydrogenation, while a recovery of properties occurs upon ageing (2). This supports evidence (11) that the presence of α' martensite (which appears during ageing) is not by itself responsible for the embrittlement. However, the occurence of α' martensite preferentially at stress concentration points, such as intersections of ε phase platlets between them and with twin and grain boundaries (5), (Mangonon and Thomas (12) may indicate that α' plays a role in crack nucleation and/or the choice of propagation path (5) (figure 2). This process is enhanced by the relative ease with which ε phase transforms within even mildly hydrogenated unstable austenite (figure 3). It has been pointed out (Hannula (13) that when ε phase is previously introduced by deformation, H induced cracks follow the γ-ε interface. It appears that this is not the case when both the ε phase and the cracks are introduced by H charging (5). Observations of cracks in hydrogenated thin foils have shown both situations, e.g., cracks along and transversal to the γ-ε borders. However in TEM samples the crack follows the path given by the γ-ε interface only in the thinner section of the sample, which may be interpreted as a particular effect in thin films (figure 4).

The second effect caused by H in unstable austenitic stainless steels, as mentioned before, e.g., that concerning hydrogenated and outgassed samples, is of major interest for the problem of fatigue. This stems from the fact that in this case the state of the surface is of utmost importance, independently of the geometry of the sample, contrary to what has been discussed for the tensile test. A fatigue test may be roughly subdivided into two different stages: initiation and propagation of cracks. The initiation stage may represent an important fraction of the total fatigue life, depending on the test conditions and on the state of the surface. As it has been shown in figure 1, a great amount of tiny cracks (of the order of several millions on a square millimeter) may come out on the surface of an austenitic stainless steel on outgassing after hydrogenation. These cracks, which appear along grain and twin boundaries as well as with a crystallographic feature within the grains, are very shallow (penetrating about 15 μm) and with a mean length of the order of 3.0 μm. One may then expect a shorter fatigue life due to a reduced initiation stage in samples containing surface cracks such as those above reffered to. This was actually verified in the tests described in figure 11, which showed 60-80% reduction in life. It is noticeable that this marked difference was obtained in tension-tension tests with very high stresses. They approach in the upper limit the condition of a static tensile test, in which the state of the surface could be expected not to play such an important role. The inserted micrograph shows opening of the

surface cracks, similar to what was presented for the samples tested in tension, and a ductile fracture.

From a practical point of view, the above described effects are to be considered with particular attention in the case of components made out of unstable austenitic stainless steel and subjected to repeated cycles of hydrogenation and outgassing in service. The tiny and shallow hydrogen induced delayed cracks herein showed could eventually grow into macro cracks and reach critical sizes capable of further reducing fatigue life and also the load carrying capacity of static loaded structures. This may be enhanced by the possibility of previous cracks acting as preferential H sinks for subsequent hydrogenation cycles.

The situation analysed in the present work, e.g., mechanical tests right after hydrogenation and after prolonged outgassing represent two out of a broader set of conditions. Others would include tests during hydrogenation and after various ageing times. As a possible particular condition, one could include a fatigue test performed shortly after hydrogenation to analyse the combined effects of HE and surface modifications.

CONCLUSIONS

1) It has been shown that hydrogenated unstable stainless steel may have it's mechanical properties altered both due to hydrogen embrittlement itself and to the effect of delayed surface cracks remaining after prolonged outgassing.

2) Quantitative measurement of the surface delayed cracks yielded an extremely high density, of the order of 20 millions per square centimeters for a moderate charging condition, with a mean length of 3μm and a depth of about 15 μm.

3) In the case of static tests of thin samples (as compared to the depth of hydrogen penetration), the mechanical properties may be deteriorated both by hydrogen embrittlement over most of the cross section and by the reduction of the load carrying capacity due to the delayed cracks in outgassed samples.

4) Fatigue life is considerably shortened by the presence of hydrogen delayed surface cracks in outgassed specimens due to a marked reduction of the crack initiation stage.

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SYMBOLS USED

α' = body centered cubic martensite
ε = close packed hexagonal martensite
$\dot{\varepsilon}$ = strain rate (s^{-1})
H = hydrogen
HE = hydrogen embrittlement
RT = room temperature
SS = stainless steel

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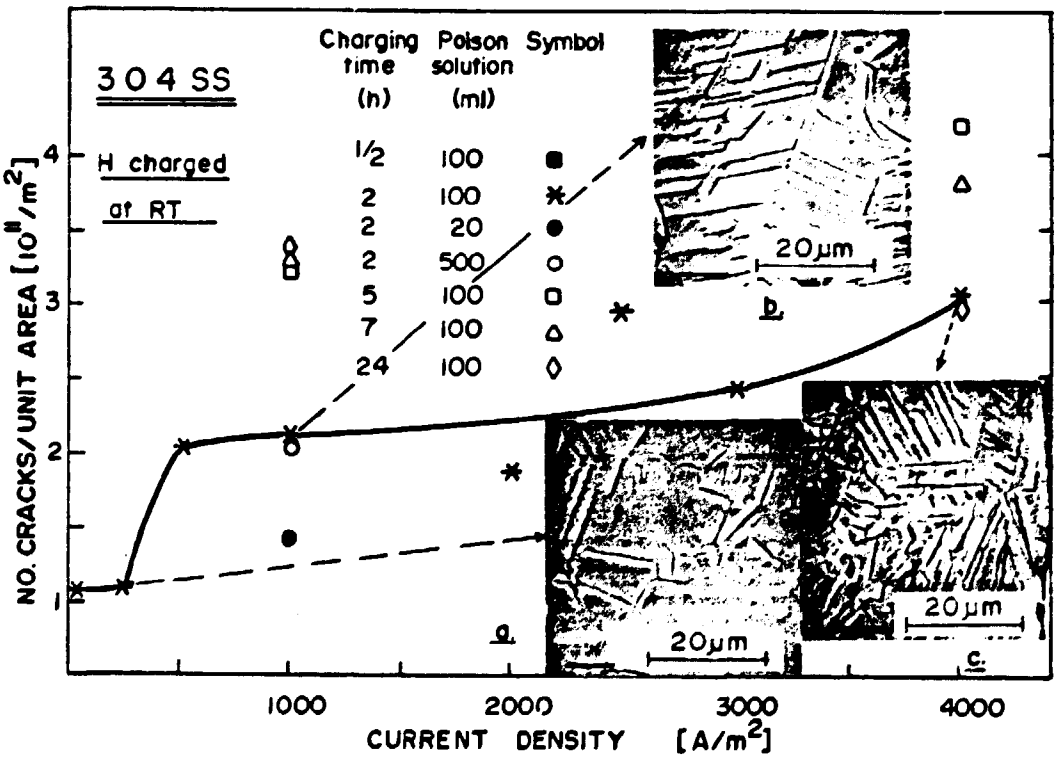

Figure 1 Variation of number of cracks per unit area as a function of hydrogen charging current density. Inserts are SEM micrographs of surface cracks

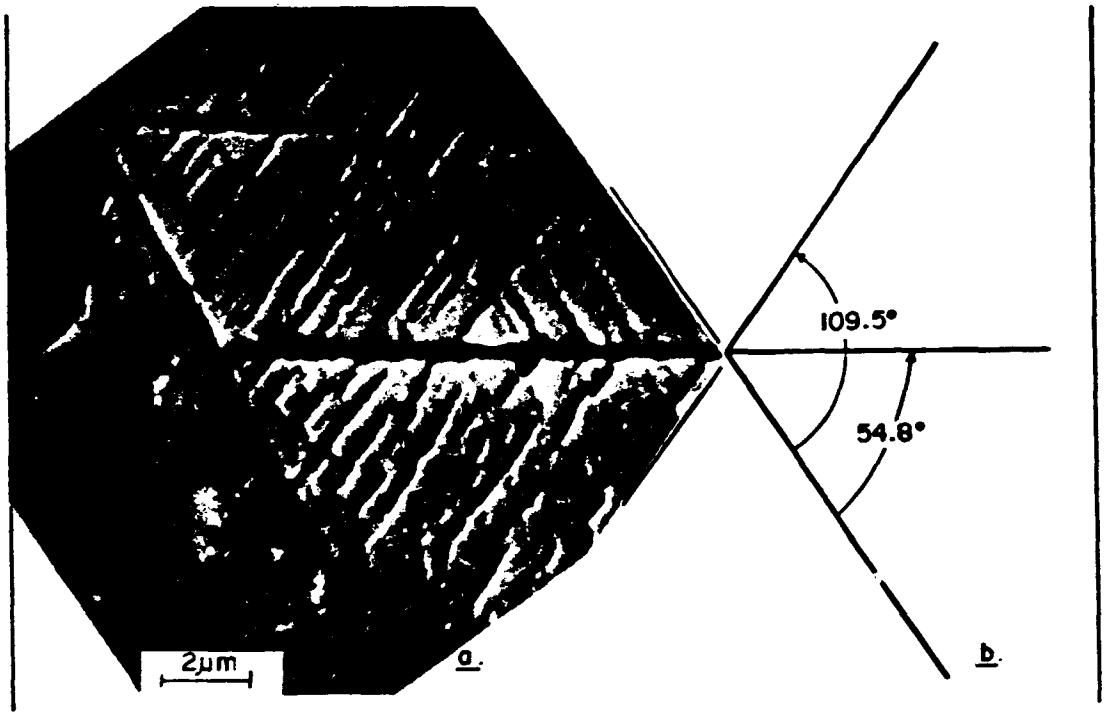

Figure 2 - a. SEM Micrograph of sample charged at 2000 A/m^2 for 2 h. ε phase at a twin. Etched with aqua regia. b. Angles between traces of planes $(111)_\gamma$ (ε phase) and the crack (ref. 4)

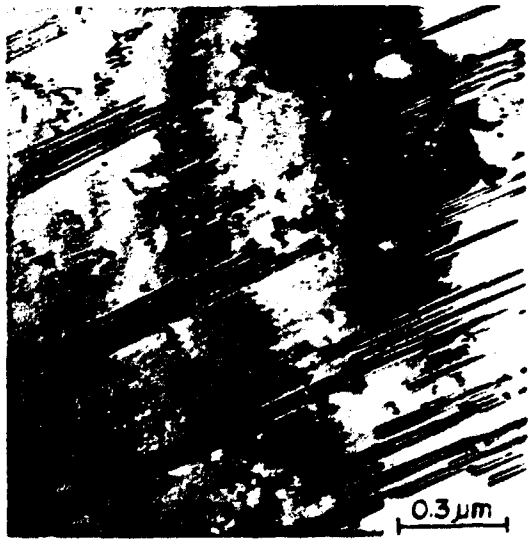

Figure 3 ε phase platlets in early stages of formation induced by H. Charged with 2000 A/m^2 for 10 minutes

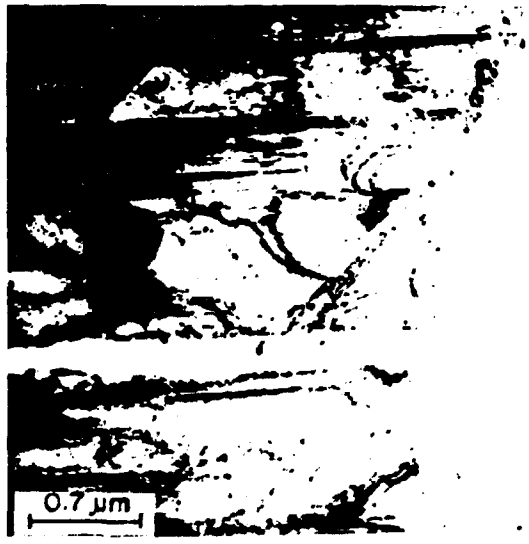

Figure 4 Crack and ε bands induced by H. Charging conditions were 2000A/m^2 for 90 minutes

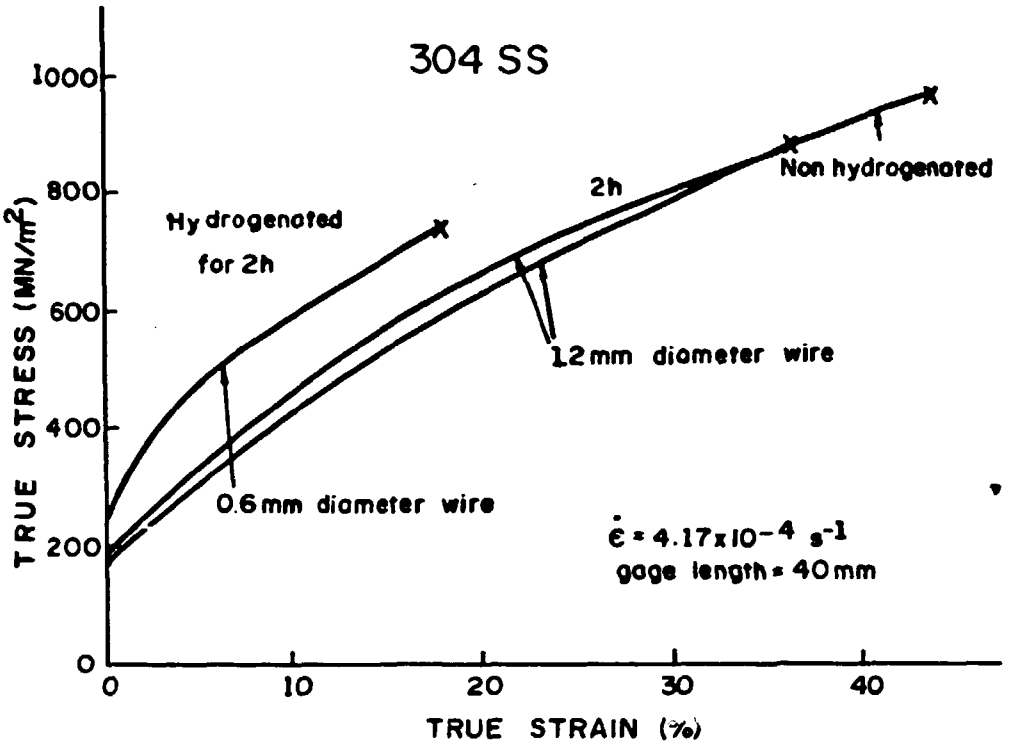

Figure 5 True stress - True strain curves for wire specimens annealed and hydrogenated with 1000A/m^2 for the specified times.

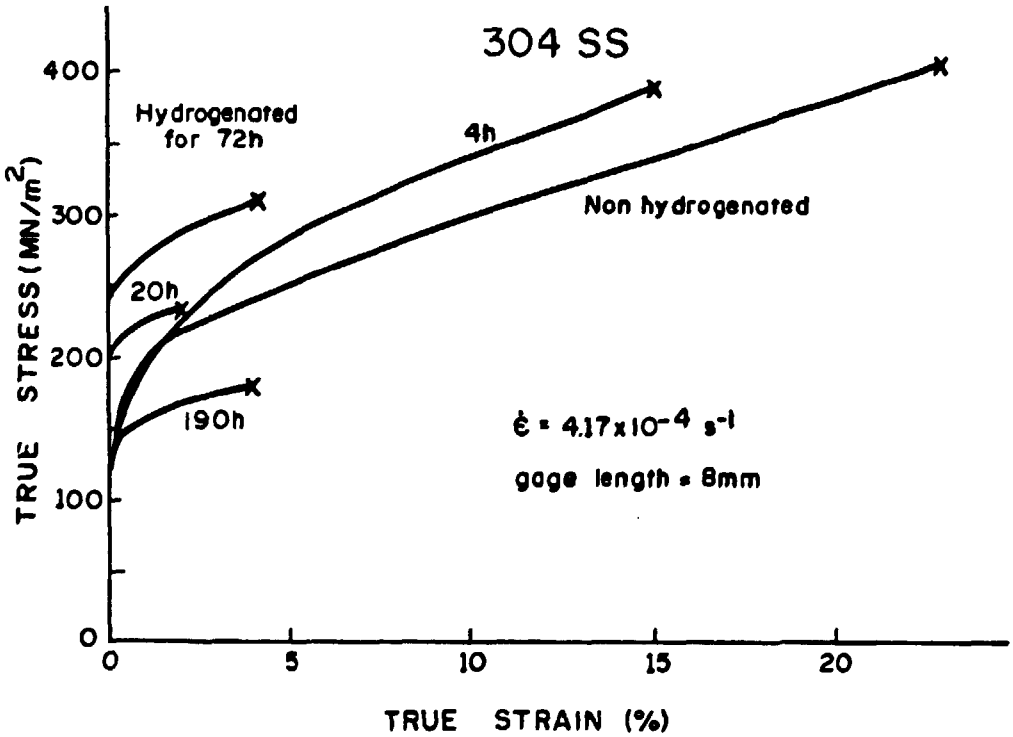

Figure 6 True stress - true strain curves for sheet specimens annealed and hydrogenated with 2000A/m^2 for the specified times.

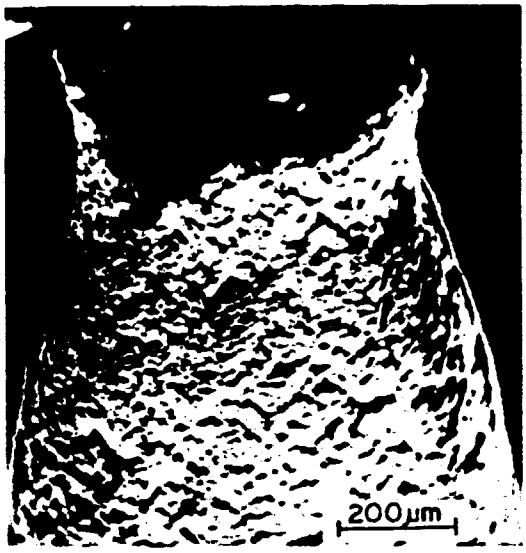

Figure 7 Wire specimen (1.2mm diameter) hydrogenated with 10,000 A/m^2 for 4 h and fractured in tension

Figure 8 Detail of H induced surface cracks of the sample shown in figure 7

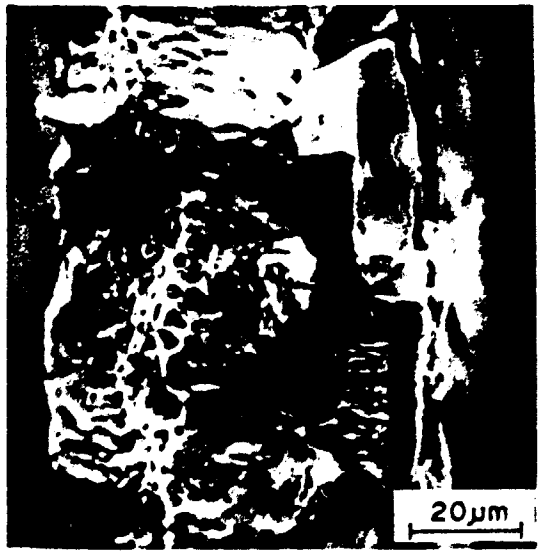

Figure 9 Fracture morphology of thin sheet sample hydrogenated with 2000A/m^2 for 20 h and fractured in tension

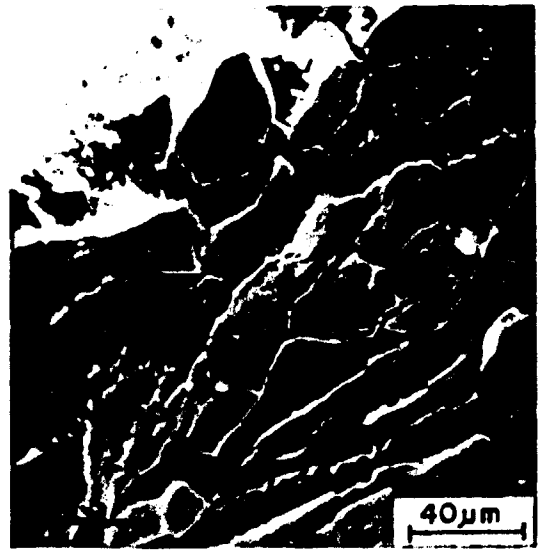

Figure 10 Lateral view of the sample shown in figure 9

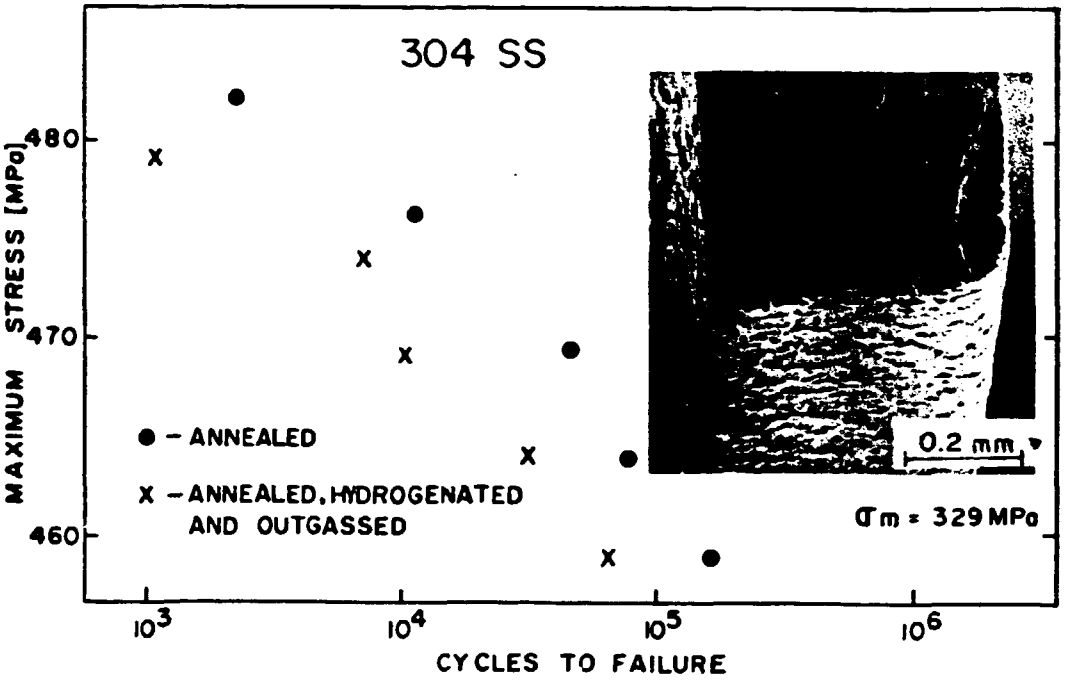

Figure 11 Fatigue life of annealed and hydrogenated samples. Insert shows typical lateral surface and fracture morphology appearence after testing

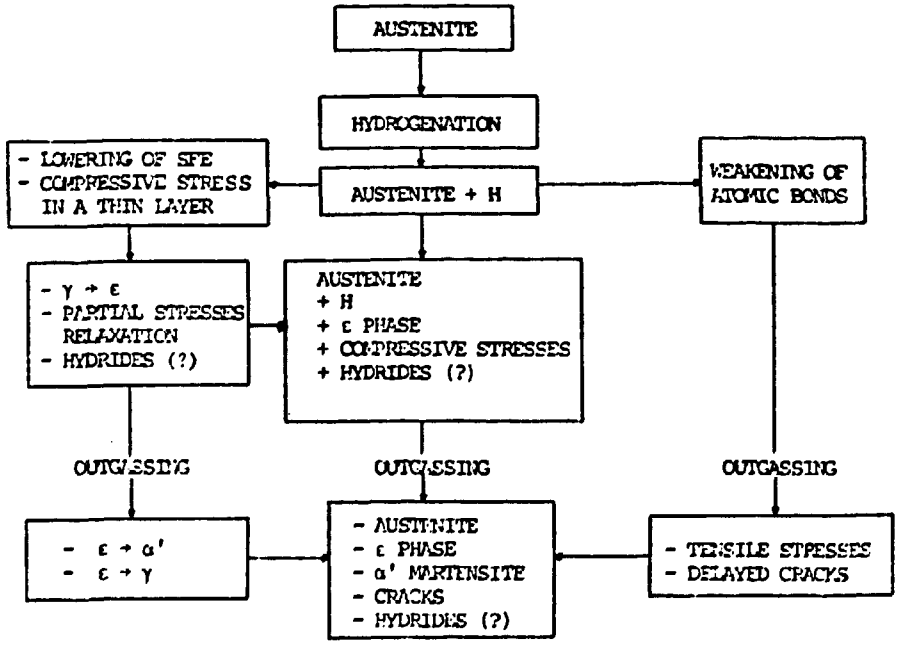

Figure 12 Schematic diagram of the phenomena occuring during hydrogenation and outgassing of an unstable austenitic stainless steel