HYDROGEN EFFECT IN STATIC OR DYNAMIC FRACTURES OF MARTENSITE-CARBIDES COMPOSITE STRUCTURES

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ABSTRACT

Complex carbide-martensite structures have been analysed through hydrogen embrittlement. The results show the great sensibility to hydrogen effect in delayed fracture tests, tensile or fatigue tests after hydrogen charging. This is an attempt to explain the reversible embrittlement by the behaviour of martensite and the entrapment of hydrogen in martensite-carbide interfaces.

KEYWORDS

Martensitic stainless steel, hydrogen, embrittlement, tensile tests, fatigue, martensite, M_7C_3 carbides, interfaces.

INTRODUCTION

Hydrogen embrittlement is now widely studied in many materials. However, very few experiments have been made on complex brittle structures with high dislocation density. In fact, contact problems require not only hard martensite but also carbides and thus hydrogen effects have to be analysed through the behaviour of a martensite-carbide composite structure. Hydrogen entrapment and embrittlement mechanism should take into account the roles of allied martensites, of carbides and also of the interfaces between carbides and martensite.

For ball bearings, hardness should be superior to 58 HRC at the running temperature, that suggests soft tempering (150 - 200° C) except for high speed steels. The classical ball bearing steel contains 1% carbon and 1.5% chromium (52 100) but for uses in corrosive or aggressive atmospheres, special steel as 440 C is needed. For this stainless material (1% Carbon, 17% Chromium, 0.5% Molybdenum) , two kinds of carbide exist in the matrix : small and rounded $M_{23}C_6$ carbide seems to have a behaviour similar to M_3C Carbide in 1% C, 1.5% Cr martensite, but the high chromium content gives the primary M_7C_3 carbide that presents complex geometries with angular points. Moreover, these carbides are often segregated in longitudinal bands, as a consequence of forging process.

The importance of thouroughly knowing the behaviour of steel under the effect of hydrogen lies in the high frequency of accelerated failures. These failures are mainly related to a lubricant effect associated to hydrogen embrittlement. The nature of lubricant (paraffinic or naphtenic mineral oils, synthetic fluids), its viscosity and additives (extreme pressure, antiwear, ...) have a dominant effect on the incidence of pitting of bearings. However, the environment - and particularly the presence of water in mineral lubricants - plays an important role.

GRUNBERG (1958), SCHATZBERG (1968), gave evidence of a considerable decrease in bearing life with the presence of water, even in very small quantities. The reduction in life can be up to 50% when contamination is made with synthetic sea water (SCHATZBERG,1969 ; FELSEN,1972). In 1977, MURPHY,(1977) and CANTLEY,(1977) corroborated the harmful role of water.

Influence of water seems very difficult to control : water can be produced by the oxidation of oils and even in "heavy" chains, water is dissolved up to several parts per million at the running temperature (SCHATZBERG, 1968).

From KRAMER's model, GRUNBERG , (1953) justified the formation of hydrogen peroxide when water - or water polluted oils - are in contact with the "fresh" metallic surfaces. These virgin surfaces would then interact with hydrocarbon to produce hydrogen.

It has then been assumed that accelerated failures of bearings can be induced by a hydrogen embrittlement due to diffusion of hydrogen into the highly stressed surface material (GRUNBERG , 1960). Many experiments showed the role of hydrogen in fatigue by the use of tritiated water (GRUNBERG , 1963), deuterium (SWETS, 1961) or electromicrofractography of failed specimens, (SCOTT, 1960, 1969).

These results have been obtained from the classical ball bearing steel (52 100) and contact fatigue behaviour of the stainless steel 440 C, in polluted oils, is not well known. SCHAFF (1977) showed a strong decrease in endurance limit, but for rotating beam tests under polluted oils and CIRCUNA (1973) gave results of bearing tests with the presence of H_2S.

In this paper, we shall study the hydrogen interaction with 440 C composite structure through mechanical tests (tensile or rotating beam tests), without any surface contact. In the last part, we shall discuss the role of the different phases and the possible mechanisms of embrittlement.

EXPERIMENTAL WORK

Steel analysis is given in table I and heat treatment in table II. Thus the structure is tempered martensite with retained austenite (12%) $M_{23}C_6$ (FCC) and M_7C_3 (hexagonal) carbide (percent of carbides is more than 30%)

TABLE 1 Chemical Analysis of 440 C Steel

C	Si	Mn	S	P	Ni	Cr	Mo
1.11	0.49	0.49	0.004	0.021	0.14	17.45	0.55

Tensile failure stress is about 1900 - 2000 MPa with a brittle fracture and 0% reduction in area.

Tensile specimens, described in Fig. 1, are drawn from 19 mm diameter bars.440 C steel is very sensitive to notch effect and furrows or scratches can induce premature failures. So, after heat treatment, specimens are ground, run in and then polished with a 4 μm alumina paste. Moreover inside of holes is polished with a running paste and surface roughness is checked under the microscope before each test.

Before setting them in tensile cathodic charging cell (Fig. 2), each specimen is degreased, rinsed, dipped in soda for 20 seconds, rinsed with distilled water, with alcohol and then dried with warm air.

TABLE II Heat Treatment of 440 C Steel

Preheating	Austenisation	Quenching	Cooling	Tempering
850°C 15min	$1010 \begin{matrix} +10 \\ +0 \end{matrix}$ 20 min	Oil	1h at - 70°C	1h at 200° C

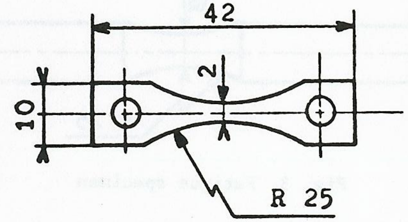

Fig. 1 Tensile specimen

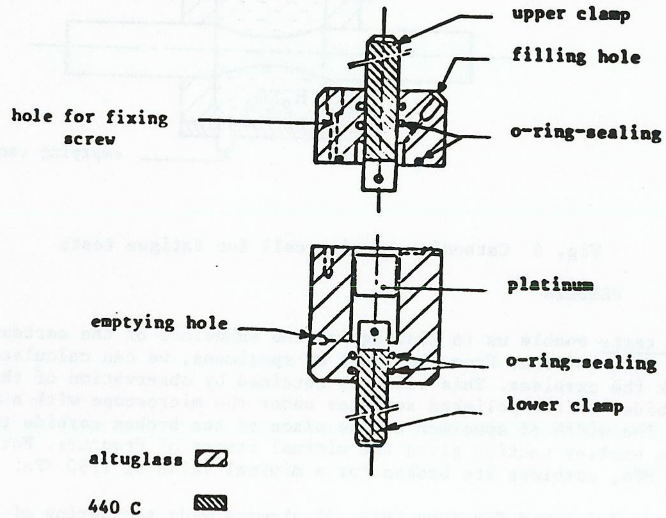

Fig. 2 Cathodic charging cell for tensile tests

Tensile specimen is the cathode of the electrolytic cell (anode = platinum) which is about 8 cm^3. Electrolyte is H_2SO_4 (1N) solution, current density has been chosen as 10 Am^{-2} and test surface of specimen is 400 mm^2. These conditions permit reversible embrittlement and avoid any internal craking or blistering.

For rotating beam tests, "Moore" type specimens (test diameter is 5 mm) are longitudinally ground (Fig. 3) and tests are done at the frequency of 100 Hz. Charging conditions are the same as for tensile tests (test area is about 500 mm^2). Charging duration is 20 min., cell (8 cm^3 - Fig. 4) is quickly emptied and rinsed with distilled water (minimal time is 15 seconds), then fatigue test is performed on the wet specimen.

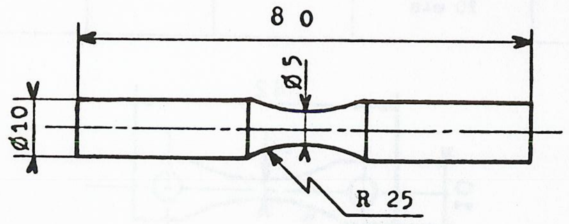

Fig. 3 Fatigue specimen

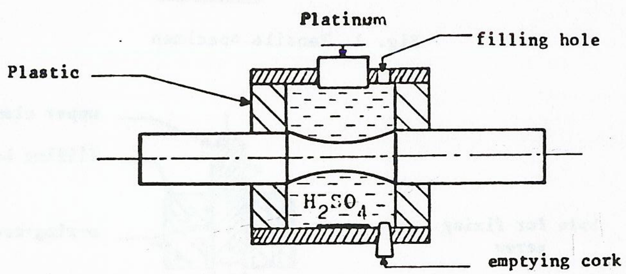

Fig. 4 Cathodic charging cell for fatigue tests

RESULTS

Tensile tests enable us to distinguish the behaviour of the martensitic matrix and that of M_7C_3 carbide. From the shape of specimens, we can calculate stresses needed to break the carbides. This value is obtained by observation of the place of broken carbides on the polished surfaces under the microscope with a magnification of 500. The width of specimen at the place of the broken carbide the most distant from the smaller section gives the minimal stress of fracture. For brittle fracture of 2000 MPa, carbides are broken for a minimal value of 1750 MPa.

The curve of delayed fracture (Fig. 5) shows a wide scattering of the results and a great sensitivity of 440 C steel to hydrogen. In fact, it is at a stress of 600 MPa that specimens can endure 4 hours without fracture and this is only 30% of the tensile strength of uncharged specimens. On the other hand, a stress of 1300 MPa results in failure in less than 10 seconds and this value is 64% of the fracture strength of uncharged specimens.

Usually the criterion of sensitivity to hydrogen in tensile tests is the ratio of reduction in area with and without embrittlement so as to take into account the effect of loss of ductility. In the case of such low tempered martensitic steel, the reduction in area is practically zero, even without embrittlement, so we

caracterised the hydrogen effect by the fracture strength.

We then studied the reversibility of hydrogen. Cathodic charging is often performed for 20 min under an external stress of 600 MPa. Two outgassing conditions were chosen, that is with or without applying the external stress (Fig. 6).

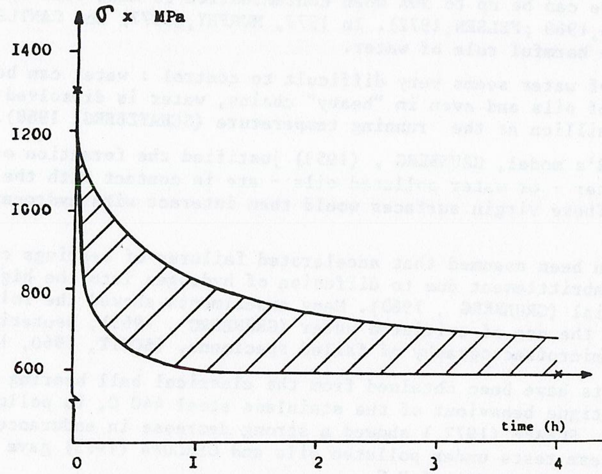

Fig. 5 Delayed fracture curve (Fracture stress of uncharged specimens is 1900-2000 MPa)

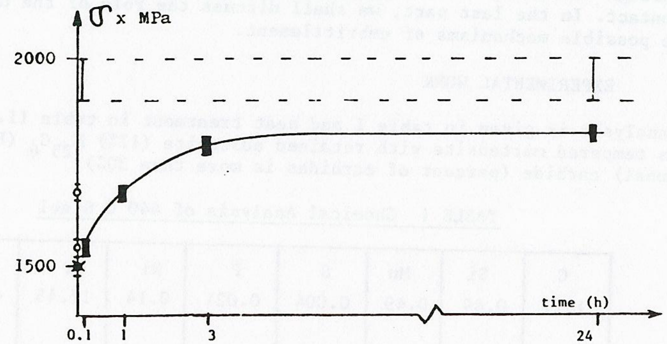

Fig. 6 Fracture stress versus outgassing time

Outgassing : with return to 0 stress
under 600 MPa

: Stress without charging or after outgassing : 1 h at 85° C
: Charging under 0 stress

From experimental conditions, it appears that the decrease in fracture stress does not depend upon the external stress applied during charging. Moreover, it is important to notice that after an outgassing period of 24 hours, the fracture stress nearly reaches the value obtained without charging during tensile tests. This last value, that is 1900-2000 MPa, is also obtained for outgassing at 85° C. Thus we have evidence of the reversibility of this hydrogen embrittlement that exists even without an external applied stress during charging.

Rotating beam tests after cathodic charging were performed at 600 MPa that is a stress slightly superior to the endurance limit in air. Hydrogen charging and outgassing are made under the same external stress of 600 MPa. The influence of the outgassing duration is given in Fig. 7. For short outgassing periods, hydrogen embrittlement is very strong and the number of cycles to failure is less than 20% of the mean one obtained without hydrogen charging. The hydrogen effect quickly becomes less sensible and with the scattering of results, it is after about 15 hours that steel recovers its properties. On the contrary to tensile tests, the stress applied during charging appears to be very important and cathodic charging without applied stress does not give a decrease in lifetime. However, this is a complex problem because long periods of charging (1 hour) lead to a strong embrittlement for an outgassing time of 30 seconds. However, the reversibility of the phenomena is faster than for charging under stress. For example, specimens outgassed during 1 hour were not embrittled at all.

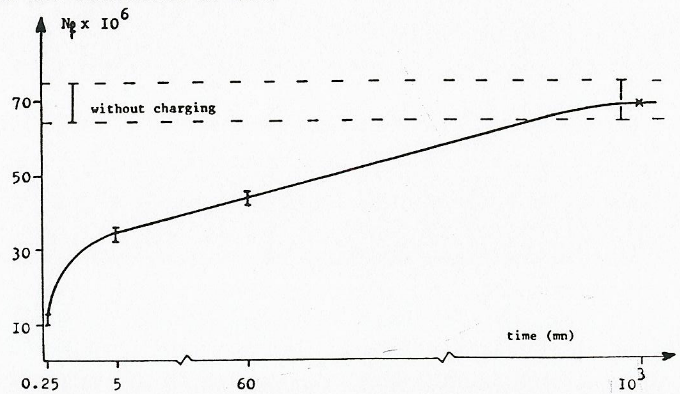

Fig. 7 Number of cycles to failure versus waiting time under 600 MPa stress

Microfractographic analysis of embrittled specimens. Specimens broken in air exhibit a great number of failed carbides and outside the main fracture plane, no crack is observed in the martensite. After hydrogen embrittlement, martensite has many cracks and the number of broken carbides is very small, compared to the number obtained in air tests. Overmore, the minimal stress, needed to break M_7C_3 carbides is then only 1400 MPa (compared to 1750 MPa in air).
Hydrogen does not give any significant change in the features of broken carbides for tensile testing. The same is for rotating beam tests in which the very fi st cracks initiate from a carbide located in the sublayers and not on the surface of specimen. The classical feature is then the bright "fish-eye" zone (VINCENT, 1976). However we notice the presence of several bright zones for the shortest lifetimes and a great number of broken carbides in the peripheric zone on the fracture plane. Both features are not observed without hydrogen charging.

DISCUSSION

The stainless steel 440 C is very sensitive to hydrogen embrittlement and results indicate a marked effect of hydrogen upon martensite as well as carbides. In fact, we must consider several mechanisms of embrittlement depending on the test, whether it is delayed fracture, tensile or fatigue after cathodic charging. Moreover these mechanisms must be related to martensite, to carbides and to the carbide-matrix interfaces.

Delayed fracture : In relation with TROIANO's theory (1960) of delayed fracture, it is worth notice that our tests are far different because our specimens have a fine surface finish and are submitted simultaneously to both hydrogen charging and mechanical stress.
Due to the intrinsic crystallographic incoherence between the M_7C_3 carbide and the matrix and to differencies between the geometry and the brittleness of both, an increase in the external stress gives decohesion at interface which can trap more hydrogen. Thus, the higher the applied stress, the shorter the incubation period during which the adsorbed hydrogen diffuses into steel and concentrates in the defects.
For higher stresses, the great number of decohesions created gives short life times. Despite this short duration, the quantity of adsorbed hydrogen is big enough compared with the numerous traps. As suggested by FUJITA (1977) for high strength steel, the first cracks seem to initiate in the numerous carbide matrix interfaces, as a consequence of internal stresses - due to martensite -, of applied stress and of stress concentrations around large defects.
The second stage of rupture, that is the"slow growing"period, is very short because of the very low plasticity of the 440 C steel. From microfractographic analysis, it appears that no crack can be observed for stresses up to 900 MPa, that is for the largest life times.
At last, we think that hydrogen effect associated with high tensile stresses can raise local stresses to a value superior to the critical stress at which dislocation motion occurs. Dislocations would then act as a hydrogen carrier and cause failure.
For this steel, being composed of martensite and M_7C_3carbides,it seems certain that delayed fracture is a consequence of a "decohesion" mechanism :first cracks are initiated in the carbide-matrix interfaces and cause failure without the slow growing period

Embrittlement and Tensile tests : During cathodic charging, hydrogen adsorbs itself at the surface of the specimen and gathers in the many traps of the material. These traps are "superficial" or internal and they can have different effects on hydrogen embrittlement. Like PRESSOUYRE (1977), we have to distinguish between good and "bad" traps. During charging, all the imperfections of steel can be filled with different intensities.
During the dynamic tensile test, two possibilities are to be considered : dislocations and carbide-matrix interfaces as they are the main source of embrittlement. The question is, is it an intrinsic embrittlement of the martensitic matrix (by the progress of dislocations), or is it the trapping of hydrogen around M_7C_3 carbides that leads to the bursting of carbides and a quick fracture through the embrittled(?) martensite ?
Even if we consider the breaking of carbides as the initial stage of fracture, dislocations can play an important role by draining their hydrogen towards the interfaces. Thus the high pressure around carbides can cause their failure, as soon as the applied stress reaches 1400 MPa, the value found as the minimal stress of fracture on the surface of broken specimens. Moreover, the hydrogen then adsorbs itself in the lips of microcracks and accelerates their propagation.
However, no result can give the conclusion of the location of the first microcracks and we cannot neglect the possibility of cracking initiation in the martensite by a decohesion phenomenon around the microdefects (platelet interfaces, prior austenitic grain boundaries, ...)
In fact, the main difficulty is in the explanation of the role played by dislocations, due to the fact that the low tempered martensite contains a very high density of dislocations regardless of tensile tests or hydrogen effects. In fact, ball bearing fatigue tests often showed that plasticity exists in hard martensite through the observation of features such as "white etched areas" or "butterflies" in the hertzian region beneath the rolling trace. (RAY, 1979).

Embrittlement and Fatigue tests : Fracture features give evidence that, similarly to uncharged specimens, charged specimens fail by the cracking of an M_7C_3 carbide, and this occurs prematurely by trapping of hydrogen in carbide-matrix interfaces. As for tensile test, dislocations can accelerate this trapping by draining of hydrogen out of low energy traps.
The great number of broken carbides outside the bright zone is the result of the propagation of the main crack in the boundary embrittled zone.
The main result of fatigue test is the obvious role of M_7C_3 carbides in the failure mechanism. This may be similar to a decohesion effect to tensile tests, but we cannot neglect a possible modification of this mechanism by the increased speed of testing in rotating beam fatigue.

Conclusion : The reversible embrittlement of the composite carbide-martensite structure is very difficult to be described. It seems necessary indeed to have evidence of hydrogen trapping both in martensite and in matrix-carbide interfaces. Experiment have to be made in a similar martensite without carbides as well as in oriented martensite-carbide structures with well defined interfaces.

High resolution autoradiographies (RAY, 1979) have shown that hydrogen is trapped in interfaces, but these autoradiographies gave us only deep traps which cannot be "bad traps" if we consider the reversibility of phenomenon. We think that embrittlement is well a consequence of the actions of dislocations and a better knowledge is to be obtained of the plasticity of such structures with high density of dislocations.

CONCLUSION

Experiments in carbide-martensite structures showed a strong hydrogen embrittlement but the mechanisms of failure are not well understood. Embrittlement may occur in martensite only, or carbide - martensite interfaces. Evidences of the role of interfaces are given but the reversibility of phenomemon seems to be associated with dislocations.

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