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A STUDY OF HYDROGEN EMBRITTLEMENT IN AUTOMOTIVE FASTENER STEELS

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ABSTRACT

Fasteners exposed to hydrogen during processing can fail unpredictably at applied stress levels well below the fracture stress. The unpredictable nature of these failure mechanisms, which may be attributed to hydrogen concentrations of the order of a few parts per million, represents a serious safety hazard to the automotive industry. In this study the susceptibility of a commercial fastener steel has been investigated. All testing was performed using a slow strain rate tensile testing technique on fatigue pre-cracked cylindrical specimens. Results describing the effect of thermal treatment and coating on the susceptibility to hydrogen embrittlement are presented.

KEYWORDS

Hydrogen embrittlement, slow strain rate, fastener steel, stress intensity.

INTRODUCTION

High-strength fasteners are widely used in the automotive industry. However, in literature it has been reported brittle failure of high strength bolts sometimes occurs. Embrittlement in fasteners may occur as a result of hydrogen introduced into the material during processing [1]. This sort of failure is normally observed in electro-galvanized high strength steel bolts and the fracture is assumed to be caused by hydrogen which was introduced during bolt manufacturing, namely, during electroplating or during acid pickling before plating. This is referred to as internal hydrogen embrittlement (IHE) or delayed failure. Hydrogen that is absorbed is diffusible within the metal lattice and tends to accumulate in areas of high stress. It is at such locations that microcracking initiates and subsequently may proceed to catastrophic fracture. The susceptibility of high strength steels to IHE depends on alloy, strength level, microstructure, and the amount and distribution of the absorbed hydrogen. It is suggested that steels with yield strengths less than 1250 MPa, i.e. which are tempered at a high temperature, are resistant to delayed fracture due to hydrogen [2]. The purpose of this work is to assess the susceptibility of a commercial fastener steel with yield stress of approximately 1100 MPa to IHE and to establish the effect of a typical low temperature annealing on the mechanical properties.

EXPERIMENTAL PROCEDURE

To evaluate the effects of low temperature annealing a series of experiments on pre-cracked specimens were performed. The materials were supplied by the Dutch fastener company Koninklijke Nedschroef Holding N.V. in a number of processing conditions, namely: a) quenched and tempered, b) quenched, tempered and electrolitically plated with zinc and c) quenched, tempered, plated and annealed. The final microstructure of the material is a heavily tempered martensite with scattered polygonal ferrite (Figure 1).

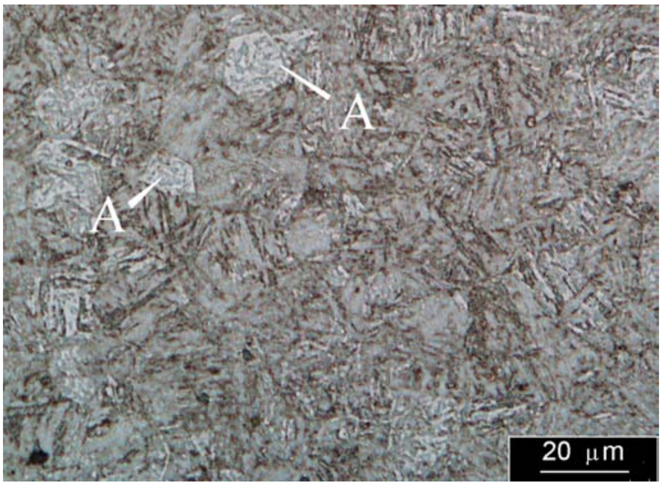


Figure 1: Photomicrograph of the tempered structure. The matrix composes mainly heavily tempered α' with some scattered polygonal ferrite *A*.

The composition of the material and mechanical properties after heat treatment are shown in the Table 1 and Table 2.

TABLE 1

COMPOSITION OF THE NEDSCHROEF STEEL

Element	C	Mn	P	S	Si	Cr	Ni	Mo	Ti	B
%	0.35	0.76	0.011	0.008	0.05	0.2	0.03	0.01	0.028	0.002

TABLE 2

MECHANICAL PROPERTIES OF THE NEDSCHROEF STEEL

Yield strength $\sigma_{0.2}$, MPa	Ultimate tensile strength σ_{UTS}, MPa	Fracture strain, ε, %	Reduction of area, ψ, %
1100	1190	13.2	63.2

The types of specimens used for mechanical testing were circumferentially notched cylindrical bar specimens (Figure 2). The fatigue precracking was performed on a four-point rotating-bending machine. For most specimens the resulting precrack was not concentric. This necessitated, in order to determine the stress intensity factors, the application of a correction for eccentricity found by *Ibrahim et al* [3].

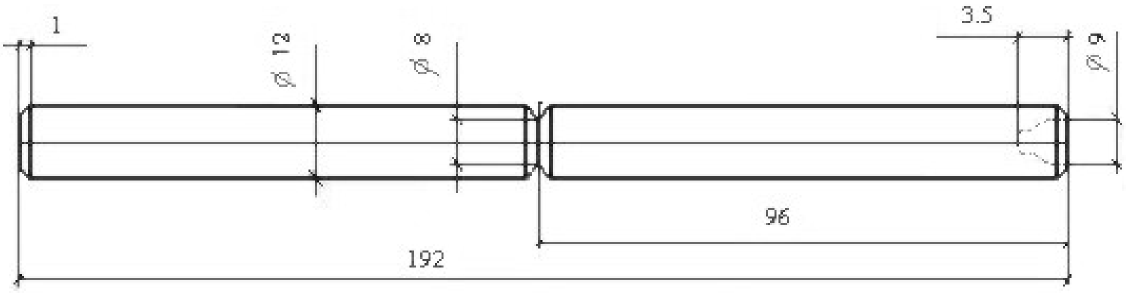


Figure 2: The specimen geometry used for fracture toughness testing

The fracture toughness tests were performed on a tensile machine in air either at the strain rate that is recommended by *ASTM E* 399-90 in fracture mechanics testing (1 mm/min) or at slow strain rate (0.001 mm/min) using fatigue pre-cracked specimens for all conditions. The test procedure of the slow strain rate test is described and compared with others in [4]. The fracture surfaces of tensile specimens were examined under both the optical microscope and scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The mechanical properties of the materials investigated, measured at a strain rate of 0.001 mm/min by tensile testing are shown in Table 3.

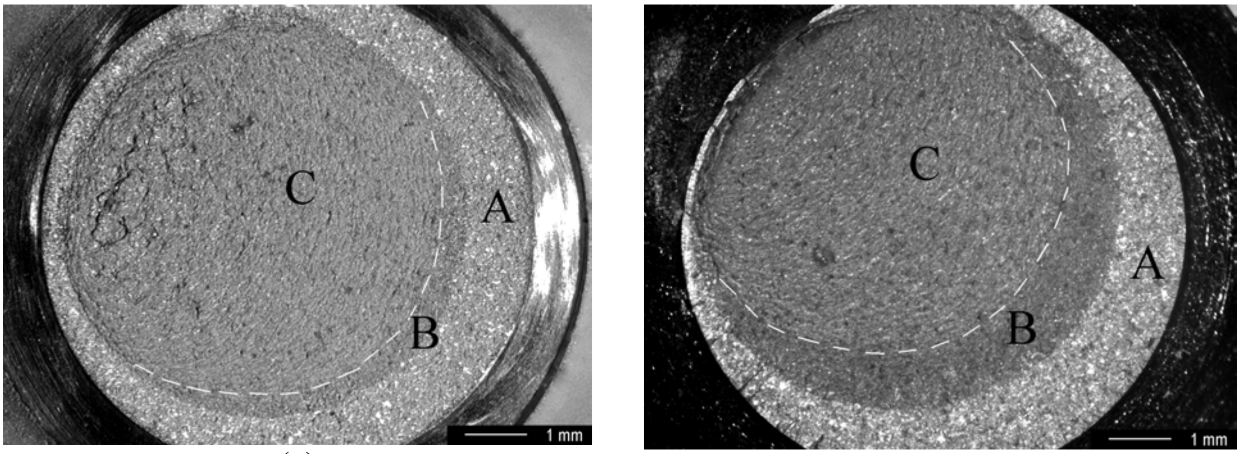
TABLE 3

THE MECHANICAL PROPERTIES OF THE INVESTIGATED MATERIAL CONDITIONS.

Material	Yield strength $\sigma_{0.2}$, MPa	Ultimate tensile strength, σ_{UTS}, MPa	Fracture strain, ε, %	Threshold stress intensity factor, K_{1H} MPa m$^{1/2}$
Quenched and tempered	1064	1190	11.1	80
Quenched, tempered and plated	1027	1155	11.7	50
Quenched, tempered, plated and annealed	1019	1151	12.5	60

The series of fracture toughness tests, performed at a tensile strain rate of 1 mm/min, did not reveal a significant difference between samples which had been plated and those which were unplated. The values of the threshold stress intensity factors K_{1H} obtained at a tensile strain rate of 0.001 mm/min (Table 3) were considerably lower than the K_{1C} value (104 MPa m$^{1/2}$).

The microfractographic investigations of the fracture surfaces of slow strain rate failure specimens revealed three zones (Figure 3): fatigue precracking, slow-crack propagation and overload failure. The region of stable, subcritical crack growth was observed for all conditions investigated (quenched and tempered; quenched, tempered and plated; quenched, tempered, plated and annealed). Microfractografic investigations of the fracture surfaces of samples tested at 1 mm/min showed no evidence of stable crack growth. Instead, the surfaces were composed of two regions: fatigue and overload.



(*a*) (*b*)

Figure 3: Fracture surface of a slow strain rate failure samples: (*a*) – unplated material; (*b*) – plated material. A – fatigue precrack; B – slow-crack propagation area; C – overload failure.

Observation of the overload region of the fracture toughness samples subjected to fracture toughness testing at 1 mm/min revealed a ductile fracture mode due to microvoid nucleation and growth (Figure 3). Fast fracture areas of the slow strain rate failure samples indicated the same ductile type of fracture.

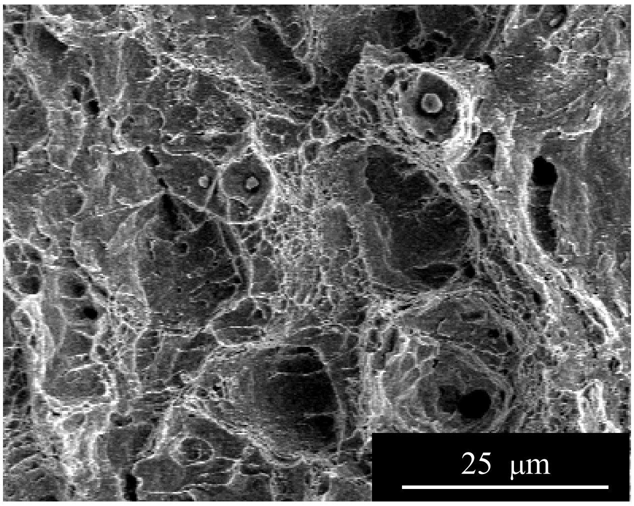


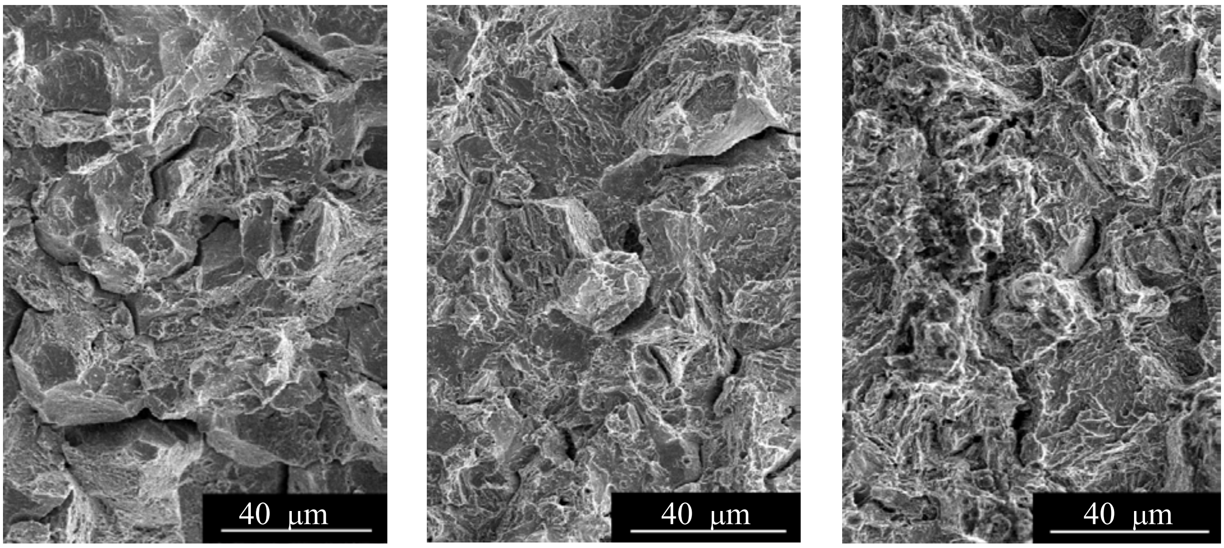
Figure 3: Fracture surface in the overload region close to the fatigue precrack for a sample failure at the 1 mm/min.

The most attention was paid to the investigation of the slow-crack propagation areas. Fracture surfaces were observed to comprise features indicative of brittle failure in this region. Many secondary cracks were also evident. It may be concluded that this embrittlement is due to either dissolved hydrogen (for the quenched and tempered material) or hydrogen introduced by the plating process (for plated material). It has been shown that for quenched and tempered material cracking was intergranular with respect to the prior austenite grain boundaries (Figure 4*a*). Whereas, the observed fracture mode for the plated material was quasicleavage (Figure 4*b*). The result shown in Figure 4 is not consistent with a known effect of hydrogen on the fracture mode. For plated material, where more hydrogen may be expected, the failure along the prior austenite grain boundaries should be preferable. The contradiction can be explained on the basis of the following assumptions:

a) at a lower hydrogen content, H occupies mainly high-angle boundary sites (i.e. prior austenite boundaries) whereas at higher H contents more hydrogen occupies low-angle boundary sites (martensite laths) or microstructural heterogeneities (carbide precipitates, manganese sulphide, etc.) within grains;

b) continuum plasticity theory predicts that even at negligibly small load a maximum stress is attained ahead of the crack tip. For crack propagation the plastic zone size must exceed a critical value, which might be related to characteristic distances such as a prior austenite grain diameter, the mean distance between carbide precipitates, etc [5].

Therefore the observed intergranular fracture for quenched and tempered material is probably a consequence of hydrogen segregation to prior austenite grain boundaries and a resulting lower cohesive force in those regions. In this case the characteristic distance may be the prior austenite grain diameter. For plated materials the hydrogen at martensite laths, carbide precipitates, etc. may play a more important role and the characteristic distance could be related to the spacing of such microstructural heterogeneties.



(*a*) (*b*) (*c*)

Figure 4: Slow-crack propagation area for quenched and tempered material (*a*), plated and unannealed (*b*) and plated and annealed (*c*) materials.

The application of a low temperature annealing on the material was observed to increase the threshold stress intensity factor (cracking started at higher stress level compared to unannealed material Table 3). The fracture surface for annealed samples was revealed to be similar to that for unplated material (Figure 4*b*).

The benefits of annealing in releasing the hydrogen introduced during plating have been investigated by *Rebak et al* [6]. It was shown that a zinc layer offered a strong barrier to hydrogen escape. In the light of this observation, the increase in resistance to hydrogen induced cracking may instead relate to a redistribution of hydrogen within the steel. According to *Townsend* [7] hydrogen, introduced during plating, is driven into deep trap sites where it loses mobility and is not available to affect embrittlement. The lower K_{1H} value for plated and annealed material compared to unplated material might be related to the generation of hydrogen at the crack tip via an electrochemical reaction with moisture in the laboratory air due to the galvanocouple ‘zinc coating – steel’. This hydrogen exacerbates the effect of any internal hydrogen which may be present.

CONCLUSIONS

1. Embrittlement, which may be attributed to hydrogen, occurs during slow-strain rate testing in air in the steel under investigation.

2. An increase in hydrogen content during the application of a Zn coating during manufacture and possibly the generation of hydrogen via cathodic reaction during testing leads to embrittlement of the steel under investigation.

3. The mechanism of subcritical crack growth observed for quenched and tempered and plated materials is different. This change in mechanism may be attributed to a change in the critical crack tip plastic zone size which relates to a microstructuraly characteristic length scale.

REFERENCES

1. Grobin, A. W. Ir. (1990) *Materials Performance* 7, 71.
2. Fujita, T. and Yamada, Y. (1977). In: *Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys*, pp. 736 – 745, Hochmann, J. and Staehle, R.W. (Eds). National Association of Corrosion Engineers, Houston.
3. Ibrahim, R.N. and Stark, H.L. (1990) *International Journal of Fracture* 44, 179.
4. Ugiansky, G.N. and Payer, J.H. (1979). *Stress Corrosion Cracking – the Slow Strain Rate Technique, ASTM STP 665*. American Society for Testing and Materials, Philadelphia.
5. Rice, J.R. (1977). In: *Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys*, pp. 11 – 15, Hochmann, J. and Staehle, R.W. (Eds). National Association of Corrosion Engineers, Houston.
6. Rebak, R.B., Muchjin, L. and Szklarska-Smialowska, Z. (1997) *Corrosion* 53, 481.
7. Townsend, H.E. (1975) *Metallurgical Transactions A* 6A, 877.