A Study of Post Plating Heat Treatment in Automotive Fastener Steels

B. Lonyuk[1], R. Hop[2], D.N. Hanlon[1], S. van der Zwaag[3], J. Zuidema[3] and A. Bakker[3]

[1] Netherlands Institute for Metals Research, Rotterdamseweg 137, 2628 AL Delft, the Netherlands
[2] Koninklijke Nedschroef Holding N.V., Techno Centre, Kanaaldijk N.W. 71, 5707 LC Helmond, The Netherlands
[3] Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

ABSTRACT: *In the automotive industry many high strength steel fasteners are zinc electroplated. The plating process is thought to be a principal cause of hydrogen embrittlement: fasteners can fail unpredictably at applied stress levels well below the fracture stress. To avoid this a hydrogen relief heat treatment after electroplating is commonly applied. In this study the effect of plating and post-plating treatments on the slow strain rate tensile fracture behaviour of two commercial steels has been investigated. Testing was conducted on fatigue pre-cracked cylindrical specimens in air. Results describing the effect of alloy selection, metallurgical processing conditions and heat treatment on the susceptibility to hydrogen embrittlement are presented. The principal conclusion drawn from this study is that post-plating hydrogen relief annealing, as specified by international standards, is not always of benefit.*

INTRODUCTION

Automotive high-strength steels for fastener applications are often protected against corrosion by electrochemical plating. This may result in the introduction of hydrogen and consequently service failure due to hydrogen embrittlement [1]. In the presence of hydrogen catastrophic failure of fasteners may occur unpredictably at applied stress levels far below the fracture stress. Hydrogen tends to accumulate at areas of high stress concentration and reduces the stress required for the initiation of fracture and the energy barrier to crack propagation.

In the automotive industry the most commonly applied method for reducing the risk of hydrogen embrittlement is a post-coating heat treatment, which is often referred as baking treatment. The severity of the embrittlement is strongly dependent on parameters such as the strength level and microstructure as well as on the amount of hydrogen introduced into the steel. The baking treatment is assumed to decrease the hydrogen concentration and consequently increase the fracture stress. According to established practice the required post-coating baking conditions (time and temperature) are dependent on the strength level of the steel. According to specifications, electroplated fasteners do not require heat treatment if made from steel with a hardness level less than 31 HR_C [2]. However, Raymond *et al*. [3] report that a standard baking heat treatment had no beneficial effect on the fracture toughness of zinc plated specimens at a hardness level as high as 52 HR_C. In this paper the results of a study of the effect of hydrogen relief treatment on two representative commercial fastener steels are reported.

EXPERIMENTAL

Circumferentially pre-cracked cylindrical bar specimens (Figure 1) were produced from two low alloy high strength steels. One is a Boron containing steel referred to as Steel A and is favoured by the european automotive fastener industry for 10.9 grade fasteners and the other, 5038 steel, is used here for the purpose of comparison since it is more typical of the steels used in the north american industry. The chemical compositions and mechanical properties of the steels are given in Tables 1 and 2 correspondingly.

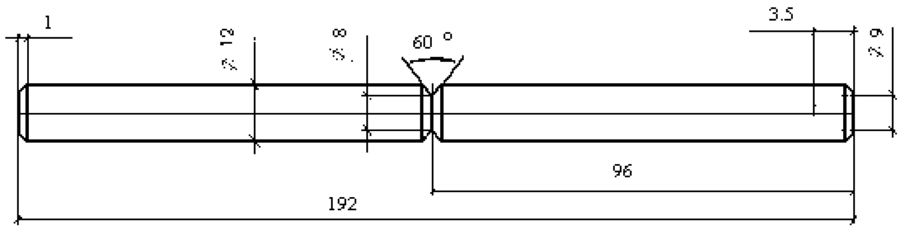


Figure 1: Specimen geometry used for fracture toughness testing.

All samples were used in the quenched and tempered condition (austenitisation at 890 °C, quenching in oil at 60 °C and tempering for 1 hour at 450 °C). In the temper used for these experiments both steels exhibit a hardness of approximately 32 HR_C and a yield stress of the order of 1100 MPa. Consequently according to standard practice a baking step should be applied prior to service (DIN 50 969). This consists of holding the plated material at 195 °C for approximately 4 hours. The microstructure of both steels was observed to be a well-tempered martensite.

TABLE 1: Chemical compositions of the steels, Wt %

Material	C	Si	Mn	P	S	Cr	Ti	B	Nb
Steel A	0.35	0.05	0.76	0.011	0.008	0.2	0.028	0.003	—
5038 steel	0.41	0.23	0.75	0.008	0.008	0.64	—	—	0.035

TABLE 2: Mechanical properties of the steels

Material	Yield stress $\sigma_{0.2}$ (MPa)	Ultimate stress σ_{UTS} (MPa)
Steel A	1100	1190
5038 steel	1098	1162

To evaluate the effect of the plating and baking treatments the materials were passed through the hardening, tempering, plating and baking cycles of a commercial process line. As a result samples in the quenched and tempered but unplated (designated QT), quenched, tempered and plated (designated QTP) and quenched, tempered, plated and baked (designated QTPB) were obtained. A few plated samples were baked for the extended times of 16 and 24 hours in order to evaluate the effect of the baking time.

The tests on fatigue pre-cracked samples were performed on a tensile machine in air at room temperature. For the pre-cracking procedure a rotating-bending configuration was used. The fracture toughness (K_{1C}) of the steel was determined according to the recommendations of *ASTM E 399-90* at an applied strain rate of 1 mm/min. Susceptibility to hydrogen embrittlement was determined by loading pre-cracked samples at a lower rate of 0.001 mm/min. The threshold stress intensity factor (K_{1H}) was calculated for the load at which the onset of the stable crack growth was detected. This was done by a method based on the compliance of the sample: the onset of crack propagation from the fatigue pre-crack tip was accompanied by an inflection from the initial linear slope of the “load – displacement” diagram. All sample were tested to failure and the fracture surfaces were observed in the scanning electron microscope (SEM).

Some of the plated samples were used for measuring the hydrogen content. Samples were sectioned to make short 12 mm diameter rods of 20 mm in length, washed thoroughly with distilled water and acetone and then dried. The hydrogen content was determined by a hot extraction technique with a H-mat 251 microprocessor-controlled analyser.

RESULTS

The results of the fracture toughness tests reveal comparable values of K_{1C} for all processing conditions (Table 3). This was of the order of 105 MPa√m for both the Steel A and the 5038 steel and it would appear that any effects of process condition on the fracture characteristics couldn't be resolved by testing at the higher applied strain rate (1 mm/min).

The K_{1H} values observed for the zinc-plated materials (Table 3) are considerably lower than the observed K_{1C} values. This indicates a degree of susceptibility to embrittlement due to internal hydrogen introduced by the plating process. The K_{1H} observed for the 5038 steel was significantly lower than that observed for the Steel A indicating that this steel is more susceptible to hydrogen cracking. This might be a result of differences in chemical compositions since the mechanical properties of both steels are similar.

TABLE 3: Effect of plating process on hydrogen embrittlement

Material	Conditions	Fracture toughness K_{1C}, MPa√m	Threshold stress intensity factor K_{1H}, MPa√m
Steel A	QT	104.3	
	QTP		54.6
	QTPB		55.6
5038 steel	QT	107.1	
	QTP		46.2
	QTPB		46.9

The K_{1H} values for materials subjected to a post-plating hydrogen relief anneal (Table 3) are comparable to the values for unbaked materials, indicating that the baking treatment is ineffective for the steels and tempers considered here. This might be due to either the application of an insufficiently long hydrogen relief treatment or may indicate that the zinc layer presents a strong barrier to hydrogen escaping during baking.

Attempts to reduce the embrittlement by extending the time of baking have been made. The results of tests conducted on samples from the Steel A indicate that extended baking up to the 24 hours yields little effect on threshold stress intensity factor (Figure 2).

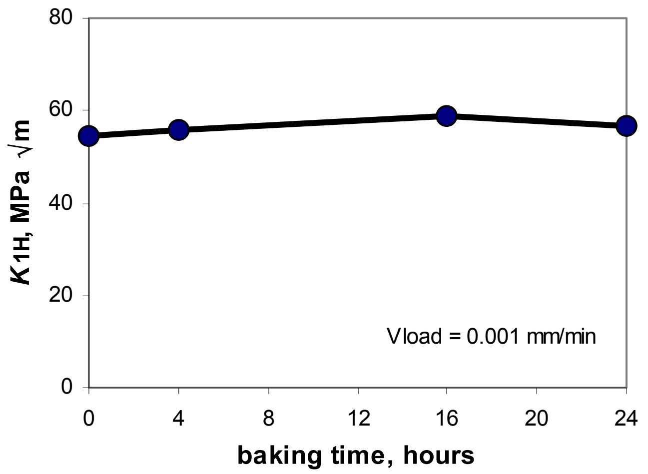
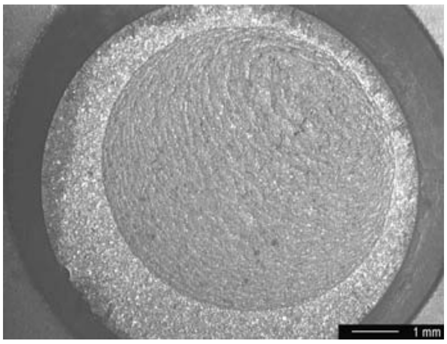
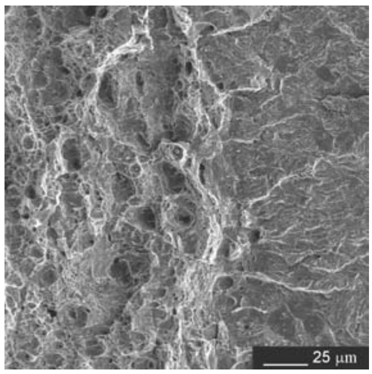


Figure 2: Effect of the baking time on the threshold stress intensity factor for hydrogen embrittlement in Steel A.

The operation of hydrogen induced embrittlement mechanisms in the materials tested has been confirmed by SEM investigations. For the materials tested at 1 mm/min the fracture surfaces comprised two distinct regions. The region of fatigue fracture was succeeded in all cases by a region of fast fracture. In this overload region the failure mode was essentially ductile. In all cases fracture is seen to occur by microvoid nucleation and coalescence as evidenced by dimple formation associated with carbides (Figure 3).



a



b

Figure 3: Macrofractography (*a*) and microfractography of dimple fracture started at fatigue pre-crack (*b*) taken from samples tested at 1.0 mm/min.

For all materials with zinc coating the fracture surfaces comprised three distinct regions. In addition to the fatigue and overload regions areas of stable crack propagation were observed (Figure 4*a*). The stable crack growth mode can be identified as quasicleavage with the appearance of a degree of intergranular character (intergranular fracture occurred along prior austenite grain boundaries as shown in Figures 4*b*-*d*). Many secondary cracks were also evident on the fracture surface.

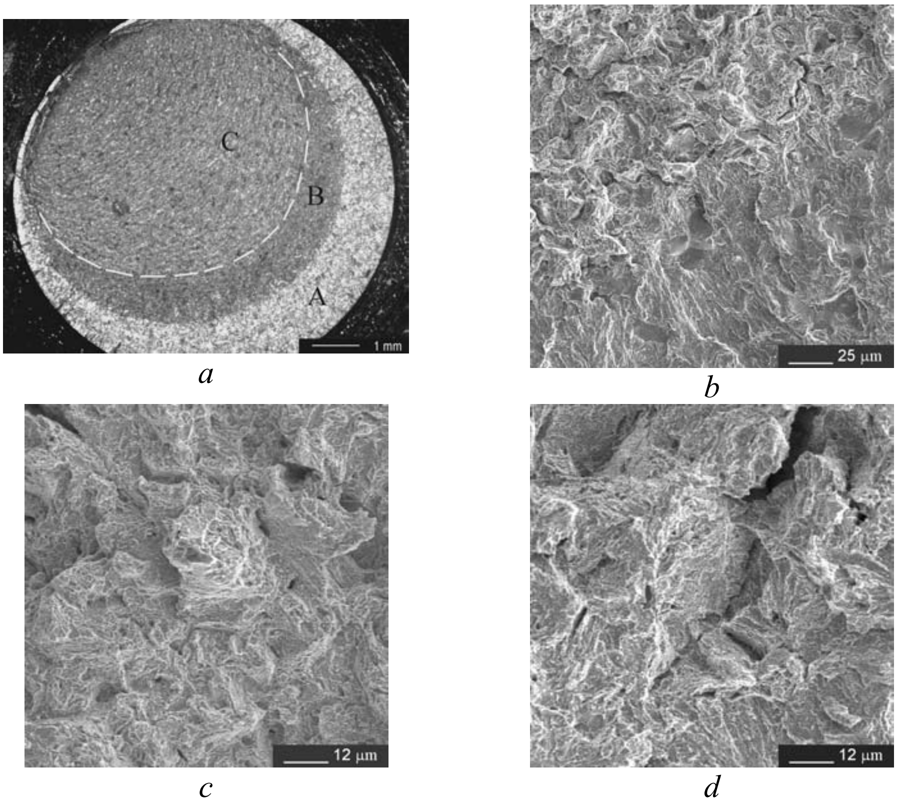


Figure 4: Stable crack propagation in zinc-plated materials broken at 0.001 mm/min; *a* – macrofractographical indication of three zones: *A* – fatigue pre-cracking; *B* – stable crack; *C* – overload; *b* – transition from fatigue to stable crack in unbaked Steel A; *c* and *d* – quasicleavage in baked for 24 hours Steel A and baked for 4 hours 5038 steel samples correspondingly.

Figure 5 shows the hydrogen content measured for Steel A samples in the unplated, plated and plated and baked (4 hours on a commercial process line) conditions. From these results it can be seen that the hydrogen content is increased after plating and that baking has little effect on the hydrogen content.

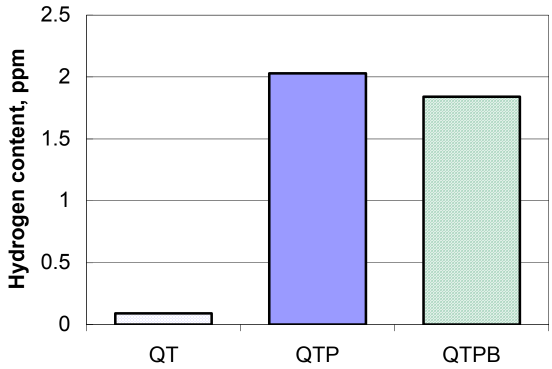


Figure 5: Effect of plating and baking on hydrogen content in Steel A samples.

DISCUSSION

Both of the steels under investigation were found to be sensitive to embrittlement by internal hydrogen introduced during plating with zinc. The unplated fracture toughness could not be restored by the application of a hydrogen relief anneal applied according to the DIN 50 969 standard recommendations for high strength steels. Previously published work by Grobin [4] reported that, in many cases, annealing for up to 23 hours or more is required in order to reduce the risk of embrittlement due to hydrogen. However, in this work a baking treatment of 24-hours duration revealed no beneficial effect for sample of the Steel A. This implies that the Zinc layer may act as an effective barrier to the release of hydrogen from the material in the temperature range up to 200 °C. Rebak *et al*. [5] found that baking treatment released only 30% of hydrogen from zinc-plated bolts. A comparable result was obtained in the present work. The hydrogen content in measured samples reduced from 2.1 ppm for plated material to 1.8 ppm for that baked for 4 hours.

In contrast, observations of a beneficial effect of baking have been reported. The positive effect of baking treatment observed by Townsend [6] was explained in terms of the trap theory. Townsend suggested that hydrogen, introduced during plating, may be driven into deep trap sites where it loses mobility and is not available to affect embrittlement. It could be assumed that the absence of an effect the baking treatment observed in present work is also related to the hydrogen distribution in the materials.

However, from the fact that hydrogen in metal lattice is always in equilibrium with the trapped hydrogen [7], it is possible that the concentration of mobile hydrogen is still sufficient to produce embrittlement.

Trapping theory may also be applied to explain the differences in fracture behaviour observed between the two steels investigated here. The higher threshold stress intensity values observed for Steel A may be considered to arise as a consequence of a higher density of strong (deep) traps compared to the 5038 steel and therefore a lower mobile hydrogen content.

CONCLUSIONS

Cracking due to hydrogen introduced during the zinc electroplating process occur in both Steel A and 5038 steel. This results in a threshold stress intensity factor which is significantly lower than the fracture toughness of the steels in question (i.e. K_{1H} is significantly lower than K_{1C}).

However, whilst hydrogen embrittlement effects were observed in both steels the 5038 steel was observed to be more susceptible than the Steel A. The Steel A exhibited a significantly higher threshold stress intensity than the 5038 steel for all conditions considered.

The baking treatment applied according to the standard recommendations for high strength fastener steels is ineffective in reducing the hydrogen embrittlement. Extending the baking time up to 24 hours produced no effect on the embrittlement of the steels investigated.

REFERENCES

1. Bickford, J.H., Nassar, S. (1998) *Handbook of Bolts and Bolted Joints*. Marsel Dekker, Inc., New York.
2. ASTM B 850-94 (1994). In: *1996 Annual book of ASTM standards. Section 2. Nonferrous metal products. Vol. 02.05,* pp. 589 – 591. American Society for Testing and Materials, Philadelphia.
3. Raymond, L. (1998) In: *Handbook of Bolts and Bolted Joints*, pp.723 – 756, eds. J.H. Bickford and S. Nassar. Marsel Dekker, Inc., New York.
4. Grobin, A.W.Ir., (1990) *Materials Performance* **7,** 71.
5. Rebak, R.B., Muchjin, L. and Szklarska-Smialowska, Z. (1997) *Corrosion* **53**, 481.
6. Townsend, H.E. (1975) *Metallurgical Transactions A* **6A**, 877.
7. Oriani, R.A. (1970) *Acta Metallurgica* **18**, 147.