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Hydrogen and Temper Embrittlement of Medium Strength Steel

Vodikova in popustna krhkost jekla srednje trdnosti

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The fracture ductility of high strength steel is strongly influenced by the presence of hydrogen, although hydrogen does not significantly affect the yield strength. The deterioration of fracture ductility is particularly evident in low strain rate tension tests, but less pronounced at conventional crosshead speeds. Microfractographic investigations of fracture surfaces of hydrogen charged high strength 5Cr-1Mo-0.3V steel from low strain rate tension test indicate that the growth and the coalescence of voids in the final stages of the fracture process are partly assisted by the decohesion of interfaces on which hydrogen is adsorbed. However, such phenomena are not observed in the experimental medium strength steel. Although a strong interaction between hydrogen and temper embrittlement was frequently observed in the alloyed steels[1,2] and though the magnitude of such effect was directly related to the degree of intergranular phosphorus enrichment[2], such synergy was not found in the experimental steel with post-martensitic microstructure.

Key words: high strength steel, medium strength steel, hydrogen and temper embrittlement, fracture ductility, low strain rate tension test

Na lomno duktilnost jekla z visoko trdnostjo močno vpliva v jeklu prisoten vodik, čeprav slednji nima znatnejšega učinka na napetost tečenja jekla. Poslabšanje lomne duktilnosti je zlasti očitno pri majhni hitrosti natezanja, medtem, ko je pri običajni hitrosti natezanja manj izrazito. Mikrofraktografske preiskave prelomnih površin nastalih pri počasnem natezanju vodičenega jekla 5Cr-1Mo-0.3V z visoko trdnostjo kažejo, da je rast in zlivanje por v končnih fazah procesa loma deloma podprta z dekohezijo medplastij, na katerih je adsorbiran vodik. Tega pojava nismo opazili pri preiskovanem jeklu srednje trdnosti, čeprav je bila pri legiranih jeklih često opažena močna interakcija med vodikovo in popustno krhkostjo[1,2] in čeprav je bila intenzivnost tega učinkovanja neposredno povezana s stopnjo interkristalne obogatitve s fosforjem[2] pa takšne sinergije nismo našli pri preiskovanem jeklu s postmartenzitno mikrostrukturo.

Ključne besede: jeklo visoke trdnosti, jeklo srednje trdnosti, vodikova in popustna krhkost, lomna duktilnost, upočasnjeno natezanje

1. Introduction

The adverse effect of hydrogen on mechanical properties has long been recognised in various metallic materials, especially in high strength steels. Hydrogen embrittlement of such steels often involves both a change in fracture mode and a reduction in ductility compared with the unhydrogenated condition[3]. It has also been established that the kinetics of hydrogen embrittlement depends on the strain rate[4-6]. However, at constant static load, the failure of high strength hydrogen charged steels, known as delayed failure, frequently occurs. This is caused by stress induced segregation of hydrogen and is characterised by the nucleation of a microcrack which then grows until it reaches a critical size, resulting in an abrupt failure. The incubation period, and the time to failure, are prolonged with a decrease in load until, at a sufficiently low load, delayed failure does not occur. Therefore, a threshold stress intensity factor K_{th} can be introduced which is considerably lower than the critical stress intensity factor or fracture toughness K_{Ic} of the uncharged steel.

Our preliminary investigations confirm that low concentrations of hydrogen (< 1 ppm by weight) in

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high strength steel have no substantial influence on its fracture toughness measured at conventional strain rate (1 mm min^{-1}). However, the low strain rate (0.1 mm min^{-1}) of hydrogen charged high strength steel decreases the fracture ductility, which indicates the existence of the threshold stress intensity factor at semi-static testing conditions[6].

Because the interaction between hydrogen and temper embrittlement was frequently observed in low and medium alloyed steels[1,2], the synergism between both embrittlements was investigated in a 5Cr-1Mo-0.3V steel with post-martensitic microstructure. The aim of the present work is therefore not only to demonstrate the applicability of low strain rate tension test in order to study the hydrogen embrittlement phenomena in high strength steel, but also to study the possible interaction between hydrogen and temper embrittlement in medium strength steel.

2. Experimental

A secondary hardening steel containing 0.38 C, 0.99 Si, 0.38 Mn, 0.012 P, 0.01 S, 5.19 Cr, 1.17 Mo, and 0.23 V (all wt-%) was used. Cylindrical tensile specimens with 10 mm dia. were machined from a forged rod after being homogeneously annealed and normalised. Some specimens were austenised at 980°C for 30 minutes in a vacuum furnace, quenched in a flow of gaseous nitrogen at a pressure of 0.5 MPa, and then tempered at temperatures of 620, 640 or 670°C. Three separate classes of yield stress, 1220, 1020 and 900 MPa respectively, were achieved.

The remaining specimens were quenched under the same conditions, then tempered twice for 2 hours at 710°C with intermediate undercooling (yield stress: 668 - 679 MPa, Charpy V-notch impact energy: 72 J), whereas some of these specimens were additionally tempered for 24 hours at 570°C, i.e. in the temperature range of reversible temper embrittlement[7,8] (yield stress: 648 - 665 MPa, Charpy V-notch impact energy: 37 J). In such cases, the experimental steel had a post-martensitic microstructure.

The cathodic charging of tensile specimens was performed for 1 h in 1 N sulphuric acid at a current density of 0.3 mA cm^{-2}. The concentration of hydrogen in some specimens (bulk concentrations) was determined using a high temperature (1050°C) vacuum extraction technique with gas chromatographic analysis. Tension tests were performed after the hydrogen charging of specimens had been completed and the specimens had been exposed to air for 24 hours. This enabled the concentrations of hydrogen to approach the residual value of approximately 0.8 ppm by weight which remained almost time independent.

The tension tests were performed at a conventional strain rate, i.e. at a crosshead speed of 1 mn min^{-1}, and at a lower strain rate, i.e. at a crosshead speed of 0.1 mm min^{-1}.

The fracture surfaces of the tensile specimens were examined in a scanning electron microscope (SEM).

3. Results

3.1 Tensile Properties

The results obtained from different strain rate tension tests for both uncharged and hydrogen-charged steel are pointed out in **Table I** and **II**. The results in **Table I** refer to the specimens which were quenched and tempered in a temperature range from 670 to 620°C with a class of yield stress of approx. 900 MPa, 1020 MPa and 1220 MPa, respectively.

Table I: Mechanical properties of uncharged and hydrogen charged steel, quenched and tempered up to high yield stresses.

Tabela I: Mehanske lastnosti nevodičenega in vodičenega jekla, ki je bilo kaljeno in popuščano na visoko napetost tečenja

Crosshead speed 1 mm min^{-1}			Crosshead speed 0.1 mm min^{-1}		
Yield stress MPa	Uniform elongation %	Reduction of area %	Yield stress MPa	Uniform elongation %	Reduction of area %
Uncharged steel					
924	8.7	52	910	8.5	51
1010	7.4	51.3	1027	6.5	50.3
1270	6.4	50	1214	6.2	50.3
Hydrogen-charged steel					
885	8.4	50.3	899	8.1	47.7
1082	7.2	49.3	1078	6.5	42.7
1209	6.1	47.3	1226	6.0	27.3

The decrease of the crosshead speed at tension had no influence on the mechanical properties of the uncharged steel, whereas it essentially influenced the reduction of area in the hydrogen charged steel (approx. 0.8 ppm hydrogen). The loss of ductility was more pronounced in steel with a higher yield stress.

The results in **Table II** refer to the steel with a post-martensitic microstructure, i.e. specimens which were quenched and tempered twice at 710°C with intermediate undercooling, and specimens which

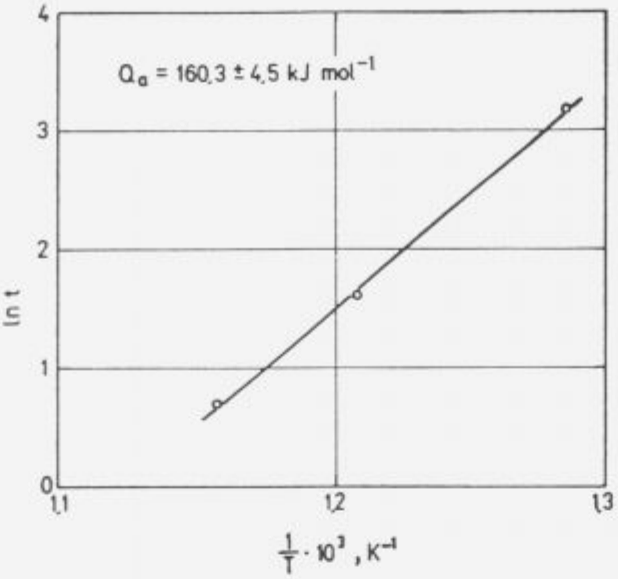

Figure 1: Evaluation of the activation energy of segregation of phosphorus according to Arrhenius equation (from Ref. 7)

Slika 1: Izvrednotenje aktivacijske energije za segregiranje fosforja z uporabo Arrheniusove enačbe (Ref. 7)

were further, additionally, tempered for 24 hours at 570°C, both with a class of yield stress of approx. 660 MPa. A weak reversible temper embrittlement of experimental steel, having a high tempered post-martensitic microstructure, was produced with additional tempering as confirmed by our preliminary investigations of the time-temperature relationship of the Charpy impact energy reduction resulting from such tempering[7]. An activation energy of about 160 kJ mol^{-1}, which is very close to that for bulk diffusion of phosphorus in ferrite, was derived from the slope of a log-log plot of time versus reciprocal tempering temperature **(Fig. 1)**.

Indeed, it has already been confirmed, using Auger spectroscopy, that in particular phosphorus segregates in this type of steel. Romhanyi and coworkers[9] found up to 6 % P and 1 % S at grain boundaries, and a strong carbon peak with carbide structure is also remarkable in Auger spectra of such steel, austenitized at 1100°C, quenched and tempered at 600°C **(Fig. 2)**. However, the segregations in our experimental steel, quenched from much lower temperature, was not so intense, and the embrittlement phenomena could be detected only by impact testing and not at all at semi-static tensile tests.

The results from both **Tables** are also shown in Diagram **(Fig. 3)**, where the tendency for hydrogen embrittlement is formulated in accordance with Morimoto and Ashida[10]:

$$\text{Degree of embrittlement} = \frac{R.A._1 - R.A._{0.1}}{R.A._1} \times 100\% \quad (1)$$

where $R.A._1$ is the reduction of area at conventional strain rate tensile test, i.e. at a crosshead speed of 1 mm min^{-1} and $R.A._{0.1}$ is the reduction of area at low strain rate tensile test, i.e. at a crosshead speed of 0.1 mm min^{-1}.

Table II: Mechanical properties of uncharged and hydrogen charged steel quenched and tempered twice at 710°C and of the same steel, additionally tempered for 24 hours at 570°C

Tabela II: Mehanske lastnosti nevodičenega in vodičenega jekla, ki je bilo kaljeno in dvakrat popuščano pri 710°C ter istega jekla, ki je bilo dodatno popuščano 24 ur pri 570°C

Crosshead speed 1 mm min^{-1}			Crosshead speed 0.1 mm min^{-1}		
Yield stress MPa	Uniform elongation %	Reduction of area %	Yield stress MPa	Uniform elongation %	Reduction of area %
Quenched and tempered twice at 710°C(Charpy V-notch energy:72 J)					
Uncharged steel					
679	12.4	55	668	11.8	55.7
Hydrogen-charged steel					
668	11.2	45	661	10.3	43.1
Quenched and tempered twice at 710°C further, additionally, tempered for 24 hours at 570°C (Charpy V-notch energy: 37 J)					
Uncharged steel					
665	11.1	51.7	664	11.7	51.7
Hydrogen-charged steel					
648	11.1	52.5	640	10.9	53

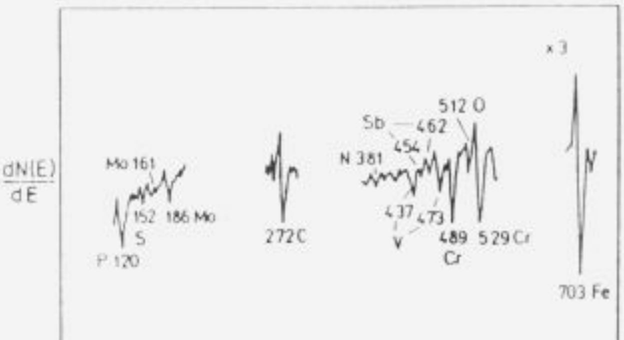

Figure 2: Auger spectrum of the intergranular surface of steel with 5 % Cr, austenitized at 1100°C, quenched and tempered at 600°C (from Ref. 9)

Slika 2: Augerjev spekter z intergranularne površine jekla s 5% kroma, austenitizirano pri 1000°C, kaljeno in popuščano pri 800°C (Ref. 9)

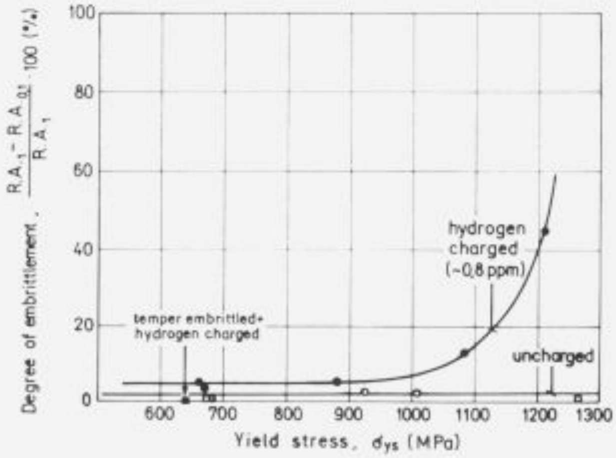

Figure 3: Degree of embrittlement of hydrogen charged steel as function of yield stress

Slika 3: Stopnja krhkosti vodičenega jekla v odvisnosti od napetosti tečenja

3.2 Fractography

The micromorphology of the typical fracture surface of hydrogen charged low-strain rate tensile specimen with yield stress of 1226 MPa, is shown in **Fig. 4** and **5**. It can be concluded that the hydrogen-induced fracture is locally ductile, tearing type of fracture with some quasicleavage details on the periphery of larger and deeper tunnel-type dimples.

The fracture surface of hydrogen charged high strength specimens obtained at conventional strain rate test and the fracture surface of hydrogen charged low- and conventional-strain rate test specimens of medium strength, i.e. the fracture surface of hydrogen charged steel, either quenched and tempered twice at 710°C or of the same steel additionally tempered for 24 hours at 570°C, are totally ductile **(Fig. 6)**. Of course, the fracture surface of

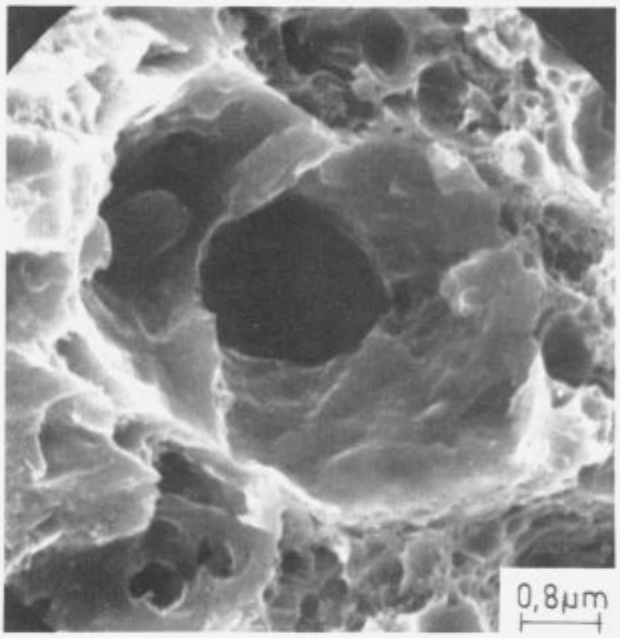

Figure 5: Detail from Fig. 4 (SEM)

Slika 5: Detail iz slike 4 (SEM)

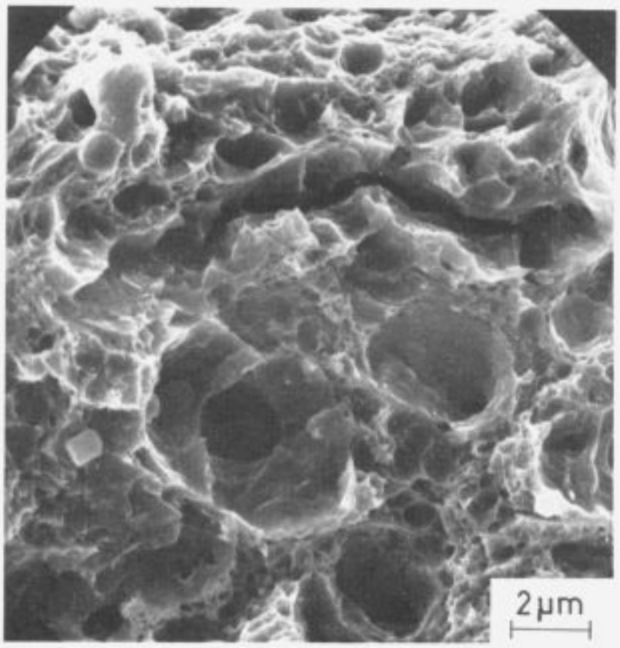

Figure 4: Fracture surface of hydrogen charged low-strain rate tensile specimen with yield stress of 1226 MPa (SEM)

Slika 4: Prelomna površina vodičenega in počasi natezanega preizkušanca z napetostjo tečenja 1226 MPa (SEM)

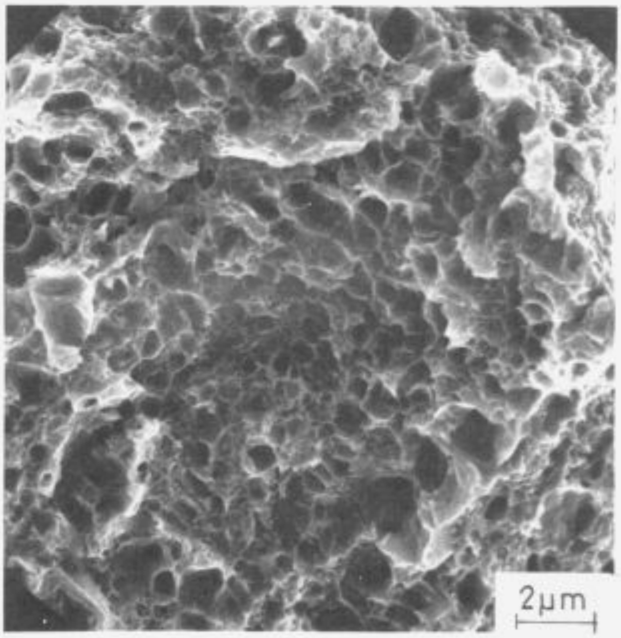

Figure 6: Fracture surface of hydrogen charged low-strain rate tensile specimen with yield stress of 640 MPa (additionally tempered for 24 hours at 570°C) (SEM)

Slika 6: Prelomna površina vodičenega in počasi natezanega preizkušanca z napetostjo tečenja 640 MPa (dodatno popuščano 24 ur pri temperaturi 570°C (SEM) additionally tempered impact specimens as for instance Charpy V-notch specimens - even uncharged - are of mixed mode. After an additional tempering at 570 °C for 24 hours, the crack propagation path changes and sporadic intergranular fracture along preaustenite grain boundaries, and quasicleavage fracture details, and single ductile tearings can be regularly observed[7].

4. Discussion

Low concentration of hydrogen in high strength steel have no significant influence on the mobility of the dislocations in earlier stages of the tensile deformation process. Hydrogen has almost no effect on the yield stress or on the uniform elongation of steel, and it only affects the reduction of area. However, the reduction of area decreases only if the strain rate is low enough to enable the Cottrell atmosphere of the hydrogen atoms pinned on the dislocations to penetrate deep into the plastic zone of the tensile specimens. Since the size l of the plastic zone of a hydrogen charged specimen is approximately half the diameter of the neck ($l = 3$ mm) at fracture, and the crosshead speed v is 1.6×10^{-3} mm s^{-1} (0.1 mm min^{-1}), a value of strain rate $\dot{\varepsilon} = v/l = 5.3 \times 10^{-4}\ s^{-1}$ is obtained. In earlier literature[11] higher $\dot{\varepsilon}$ values are quoted for stainless steel. However, the investigations performed by Nakano *et al.*[12] on hydrogen charged steel with yield stress of 500 MPa using low strain rate measurements show that at sufficient concentration of hydrogen in steel the reduction of area asymptotically approaches the lower value even at a critical strain rate of $\dot{\varepsilon} = 10^{-4}\ s^{-1}$, which is of the same order of magnitude as in the present investigations.

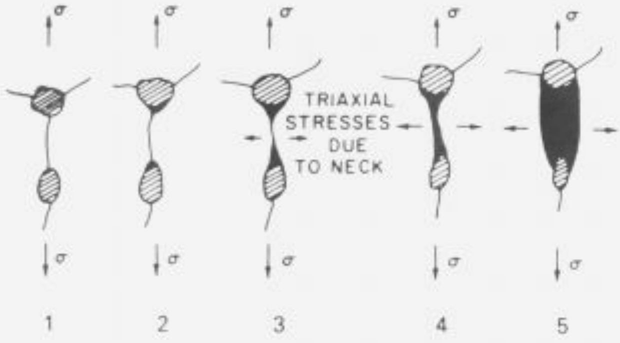

Figure 7: Schematic representation of microvoid formation, growth, and coalescence along grain boundaries in which hydrogen is adsorbed (from Ref. 13)

Slika 7: Shematski prikaz tvorbe mikropor, njihove rasti in zlivanja vzdolž meja zrn, na katerih je adsorbiran vodik (Ref. 13)

Microfractographic examinations show that hydrogen charged low strain rate tensile specimens exhibited some interfacial separation on the fracture surface. The growth and the coalescence of microvoids along the grain boundary, schematically shown in **Fig. 7**, are accelerated by separating internal interfaces where hydrogen is adsorbed[13,14].

Microvoid coalescence and the separation of internal interfaces due to adsorbed hydrogen become operative when the triaxial stress state in the narrow neck of the tensile specimen is formed (**Fig. 7**, sequences 3 to 5), resulting in the "condensation" of the last stage of plastic deformation in the low strain rate tension testing of high strength hydrogen charged steel. However, such phenomena are not observed in medium strength steel. Although a strong interaction between hydrogen and temper embrittlement was frequently observed in such alloyed steels[1,2] and though the magnitude of such effect was directly related to the degree of intergranular phosphorus enrichment[2], such synergy was not found in the experimental steel with post-martensitic microstructure. In studying the influence of bulk and grain boundary phosphorus content on hydrogen induced cracking in low strength steel, Dayal and Grabke[15] also found that the effect of phosphorus is related to the bulk content and not to the grain boundary concentration. Obviously, in the case of the experimental steel with post-martensitic microstructure, the influence of hydrogen decreases and becomes more complicated due to some particular effect of the microstructure. In agreement with Charbonnier and Pressouyre[16] these results show that the nearer is the actual microstructural state to the state of the thermodynamical equilibrium, the less susceptible is the steel to hydrogen embrittlement.

5. Conclusions

The relevance of the low-strain rate tension test to establish the hydrogen embrittlement susceptibility of both high and medium strength steel is demonstrated. The applicable **formula (1)** for the estimation of such susceptibility[10], based on the reduction of area measurements at the low and the conventional strain rate tensile test, is also successfully adopted. The synergism between hydrogen and temper embrittlement was not found in the experimental, additionally tempered steel with post-martensitic microstructure. On the contrary, such steel is less susceptible to the influence of hydrogen, due to some particular effects of the microstructure which is close to the thermodynamical equilibrium.

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