

THE INFLUENCE OF HYDROGEN IN SOLID SOLUTIONS OF SPRING STEEL

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This paper is concerned with the question of the brittle cracking of spring steel, which can occur already in the early stages of steel processing, i.e. during rolling, during the mechanical cutting of rolled profiles, or during any other type of mechanical manipulation where the harmful effect of remaining hydrogen has been observed. In order to investigate this question in greater depth, mechanical tests and fractographic analyses of the fracture surfaces were performed on cathodically hydrogenated test specimens of two types of spring steel, with and without alloyed nitrogen, in order to determine the critical concentration of hydrogen below which a relatively ductile fracture surface occurs, with good resistance to brittle cracking, and above which hydrogen embrittlement occurs.

Key words: *spring steel, hydrogen, hydrogen embrittlement, critical hydrogen quantity*

Utjecaj vodika u krutoj otopini čelika za opruge. Ovaj rad odnosi se na problematiku krtoq pucanja čelika za opruge već u njegovoj ranoj fazi prerade: pri valjanju, strojnom rezanju valjanih profila, ili kod neke druge mehaničke obrade, gdje je bio uočen škodljiv utjecaj zaostalog vodika. Pomoću uzoraka koji su bili katodno vodičeni, mehaničkog ispitivanja tih uzoraka i fraktografske analize prelomnih površina, bila je definirana kritična količina vodika. Ispod te kritične količine prisutna je još relativno žilava prelomna površina i dobra otpornost prema krhkom pucanju radi vodikove krhkosti. Iznad te vrijednosti, manifestira se vodikova krhkost.

Ključne riječi: *čelik za opruge, vodik, vodikova krhkost, kritična količina vodika*

INTRODUCTION

Damage caused by the action of atomic hydrogen in metals can be classified as damage caused by the environment, which is often, but not necessarily, linked to stresses in the material. Such damage occurs in specific alloys or specific groups of alloys in different forms, such as brittle cracking, reduced ductility, blistering, the occurrence of hydrides, etc. [1, 2]. Damage caused by hydrogen does not depend just on the environment and on stresses in the material, but also on the type of alloy, on its chemical composition and crystalline structure, and on the numerous faults in the crystal lattice, among which dislocations have the most important effect [3]. The susceptibility of steel to hydrogen embrittlement is also strongly affected by the way in which the crystal planes are occupied by atoms, as well as by the inter-atomic distances, the electron configuration, the way in which the metal system has crystallized, the microstructure, type, mode of distribution and quanti-

ties of individual phases and other components, the state of the surface, the strength characteristics, the toughness of the material [4]. Thus the problems with the material are very complicated. They are connected with the events occurring at the electrode surfaces (if what is involved is the corrosion or electrochemical source of hydrogen as the most frequently-occurring reason for the hydrogenation of material), as well as with the processes which involve the penetration of atomic hydrogen into the metal, with the transport of this hydrogen into the interior of the metal and its destructive action in the crystal lattice. The individual mechanisms of the transport of atomic hydrogen into the crystal lattice are relatively complicated and connected to many interdependent factors. Thus the transport of hydrogen depends on the microstructural stress gradients, on the hydrogen's interaction with the dislocations, on the possibility that the hydrogen is caught in a "trap" belonging to the crystal lattice, etc. The material becomes sensitive to hydrogen whenever a critical quantity of the latter diffuses into certain regions, whereas in the case of lesser quantities a crack will neither be initiated nor will it progress, thus eliminating the possibility of hydrogen embrittlement. These potentially threatened areas are the

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already mentioned traps of all kinds [5]. Thus the modern theory of hydrogen embrittlement depends upon the occurrence of trapped hydrogen. It was on the basis of this that the theory of traps was developed, according to which a crack occurs when the quantity of trapped hydrogen at the location of the crack exceeds some critical value. The hydrogen will diffuse into the metal at those locations where the smallest activation energy is needed, and in the metal it can occur as:

- interstitially dissolved atomic hydrogen, which occurs in the form of an atomic cloud, which has the tendency to occupy traps or migrate outwards,
- atomic hydrogen, which is caught in traps,
- molecular hydrogen, which occurs with the recombination of atomic hydrogen at favourable locations (traps),
- hydrogen which is bound in the form of hydrides.

It is quite clear that molecular hydrogen is no longer mobile. It has performed its work by changing into a gas in such a way that the molecules of gas apply a pressure to the neighbouring environment (Zappfe's mechanism), in which it can cause microcracks, and through the uniting of such cracks, even macrocracks. The atomic hydrogen which is caught in a trap can, under favourable conditions, bind itself to another atom of hydrogen, which has been caught in the direct vicinity, into a molecule, or, in the case of a sufficiently large activation energy (e.g. in the case of the adding of heat) it can break away and become mobile again. It is this mobile hydrogen that is particularly dangerous, since, at favourable locations, i.e. at traps which are capable of accumulating the largest quantities of hydrogen, it can reduce the binding force between the atoms of the metal, or it can be bound into molecular hydrogen, or, in certain metal systems, it can result in the formation of dangerous hydrides. Due to the action of mobile hydrogen, delayed fractures can occur, which are one of the most frequently observed results of the operation of hydrogen over a certain period of time [6]. Delayed fractures actually represent the slow growth of a crack, which occurs due to the action of the excess part of the hydrogen, which cannot be dissolved in the crystal lattice.

This research work is concerned with the effect of hydrogen in steel for the production of springs. The negative effect of hydrogen is manifested already in the early stages of steel processing, during mechanical cutting and other types of mechanical manipulation (shaping) of the ingots, i.e. of thick, thermally untreated slab-like profiles (Figure 1.). Hydrogenation of steel occurs during the remelting and refining of the melt, when the solubility of hydrogen in the iron is high. In the stage in which continuous hardening of the ingots occurs, some of the hydrogen diffuses out of the steel, but a certain quantity of so-called internal or remaining hydrogen remains, and this is the hydrogen which is responsible for the hydrogen embrittlement of



Figure 1. **Brittle cracking of rolled profiles in mechanical cutting due to remaining internal hydrogen**

Slika 1. **Krhko pucanje valjanih profila pri strojnom rezanju radi zaostalog vodika**

the steel. In order to avoid such conditions, it is necessary, immediately after continuous casting has taken place, to reduce the quantity of hydrogen which is dissolved in the solid state, which can be done by diffusion annealing of the ingots at a constant temperature of 650 °C, which was selected for steels of this kind. However, within this context the question arises as to what annealing times are needed in relation to the concentration of interstitially dissolved atomic hydrogen, or to the concentration of atomic hydrogen caught in traps. It is a fact that the concentration of hydrogen in the ingots varies from heat to heat, and for industrial purposes it is necessary to have an exact prediction of what annealing time is needed, if the quantity of hydrogen in the solid solution of the metal changes.

MATERIALS AND METHODS OF INVESTIGATION

The basic material for the tests consisted of two types of spring steels in the form of thermally untreated, thick slab-shaped profiles, having dimensions of 100 × 50 mm (width × thickness) and a ferritic-perlitic microstructure. Smaller square-shaped profiles having dimensions 22 × 22 mm were cut out of these rolled profiles and annealed for 36 h at 650 °C with the purpose of eliminating the hydrogen which remained in the steel after continuous casting of the slabs. The test samples without hydrogen were later electrochemically hydrogenated to the desired concentration of hydrogen.

The chemical composition of the investigated steels is shown in Table 1.

Table 1. **Chemical composition of the investigated steels (by mass %)**

Tablica 1. **Kemijski sastav ispitivanih čelika (masa / %)**

Steel	C	Si	Mn	P	S	Cr
50CrV4	0,56	0,26	1,09	0,016	0,006	1,17
50CrV4+N	0,53	0,26	1,03	0,014	0,009	1,12
Steel	Mo	Ni	Al	Cu	V	N
50CrV4	0,03	0,13	0,030	0,25	0,13	0,0075
50CrV4+N	0,04	0,17	0,024	0,23	0,13	0,0160

Note: the steel 50CrV4+N contained alloyed nitrogen.

The critical quantity of hydrogen, above which rapid worsening of the mechanical properties (particularly ductility) occurs due to hydrogen embrittlement, was determined by hydrogenating tensile test specimens having a diameter of 6 mm.

The conditions under which electrochemical hydrogenation was performed were the following:

- a de-aerated solution of 1N H₂SO₄ + 10 mg As₂O₃ /l, 20 °C,
- electrochemical hydrogenation by means of cathodic polarization.

Numerous preliminary tests were performed in order to determine which hydrogenation conditions are needed to achieve a suitable amount of atomic hydrogen in the steel during cathodic charging of the working sample. Thus the kinetics of the process of hydrogenation of the steel are defined by the cathodic overpotential. This means that the process does not operate completely with the formation of H₂ on the surface of the steel:



but is a combined reaction consisting of the intermediate stages:



or



Since reaction (2) is the slowest of above-stated reactions, the process does not take place completely according to reaction (1), but part of the atomic hydrogen migrates into the metal.

The quantity of hydrogen in the steel after hydrogenation was determined using the vacuum extraction method and the equipment Eltra Oh-900 - Analyzer with Electrode Impulse Furnace for Hydrogen and Oxygen in Steel.

DETERMINATION OF THE CRITICAL QUANTITY OF HYDROGEN IN THE STEEL AND ITS EFFECT ON THE MECHANISM OF HYDROGEN EMBRITTLEMENT

Viewed from the standpoint of hydrogen embrittlement, where the hydrogen traps have the dominant role, the atomic hydrogen, which occurs in the steel in the form of a Cottrell atmosphere, causes local damage in the metal if a critical quantity of hydrogen is caught in the traps. The critical quantity of hydrogen depends on the ability of the microstruc-

ture to dissolve interstitially a larger or smaller quantity of hydrogen, on the type of traps, on the number of traps, and, particularly, on the interaction energy between the hydrogen and the traps. Some steels can be hydrogenated relatively quickly, so that it is necessary to get rid of the hydrogen effectively by means of suitable annealing before it can cause damage (brittle areas and cracks).

Table 2. **The effect of the time of cathodic polarization (i.e. the time of hydrogenation) and the amount of hydrogen on reduction in area and on the strength characteristics of the steel 50CrV4**

Tablica 2. **Utjecaj vremena katodne polarizacije (vremena vodičenja) i udio vodika na kontrakciju i vlačnu čvrstoću čelika 50CrV4**

Test specimen	Duration of cathodic polarization / h	Reduction in area Z / %	Elongation A / %	Tensile strength N/mm ²	Average amount of H / ppm
Basic state	0,00	39,7	17	835	-
1	0,50	34,7	17	796	0,33
2/1	0,75	32,2	17	799	0,34
2/2	0,75	33,0	16	804	0,34
3	1,00	26,5	13	811	0,63
4	1,25	13,9	11	800	0,70
5	1,50	10,8	9	794	0,95
6	3,00	5,0	5	784	1,28

The influence of hydrogen on hydrogen embrittlement is most frequently defined by determining the reduction in area of the hydrogenated and failed tensile test specimens, followed by the fractographic analysis of the fracture surfaces.

In Tables 2. and 3. are shown, for both investigated steels, the relationship between the concentration of ab-

Table 3. **The effect of the time of cathodic polarization (i.e. the time of hydrogenation) and the amount of hydrogen on reduction in area and on the strength characteristics of the steel 50CrV4+N**

Tablica 3. **Utjecaj vremena katodne polarizacije (vremena vodičenja) i udio vodika na kontrakciju i svojstva čvrstoće čelika 50CrV4+N**

Test specimen	Duration of cathodic polarization / h	Reduction in area Z / %	Elongation A / %	Tensile strength N/mm ²	Average amount of H / ppm
Basic state	0.00	51.7	23	784	-
1	0.50	35.8	18	774	0.83
2	0.75	32.3	16	768	1.01
3	1	30.9	15	762	1.84
4	2	32.1	14	768	1.60
5	3	31.0	15	780	2.50
6	5	29.5	14	773	4.05

sorbed atomic hydrogen and the time of cathodic polarization, and the effect of hydrogen on reduction in area and strength properties, whereas a comparison of the resistance of the two steels to hydrogen embrittlement is shown in Figure 2. The critical quantity of hydrogen was defined on the basis of reduction in area, and on an esti-

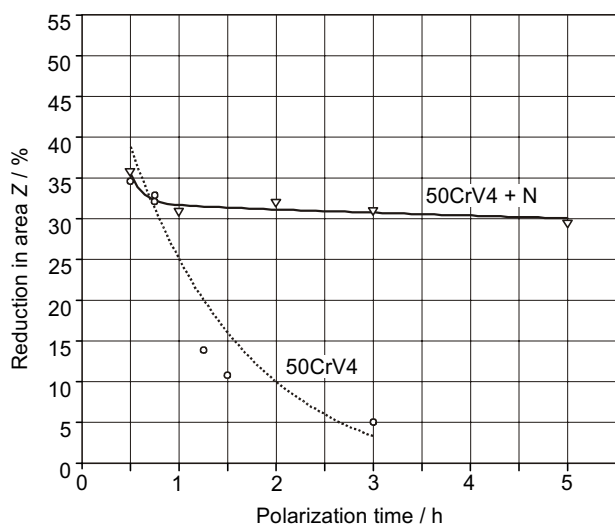


Figure 2. Comparison between the two investigated steels with respect to their resistance to hydrogen embrittlement

Slika 2. Usporedba oba čelika obzirom na otpornost prema vodikovoj krhkosti

mate of the proportion of the still ductile fracture surface of the tensile test specimen with a diameter of 6 mm. In order to permit migration of the hydrogen to the traps, which make possible a sufficiently high concentration of hydrogen in their vicinity, which is sufficient to cause hydrogen embrittlement, the hydrogenated test specimens were loaded in a tensile testing machine with an extension rate of $1,7 \cdot 10^{-6}$ m/s. Such a slow rate of loading in the region where final failure takes place represented the process of brittle reworking of the hydrogenated steel. The diameter of the fracture plane was determined using an optical measuring device, and not with much less accurate callipers. This made possible the determination of those small differences in reduction in area which occur with the increasing of the concentration of hydrogen in the case of cathodic polarization (the test specimens were hydrogenated for different periods of time), and of those differences which occur in the case of relatively brittle, strongly hydrogenated test specimens. Values for reduction in area were, for this reason, determined to an accuracy of one-tenth of a percent.

DISCUSSION

The first and most significant finding is connected with the rapid drop in reduction in area of the steel 50CrV4 - i.e. of its toughness, or more exactly, its resistance to hydrogen

embrittlement, with the increasing of the quantity of dissolved hydrogen in the crystal lattice. In the case of a relatively small concentration of dissolved hydrogen, amounting on average to 1.28 ppm, the reduction in area is small ($Z = 5\%$). This means that the steel is very sensitive to the action of the hydrogen. Under the influence of hydrogen, thermodynamically very unstable brittle areas are formed, through which the rapid growth of a leading crack can occur, with the coalescence of several smaller cracks. Later fractographic analyses of the fracture surfaces showed that, as the concentration of hydrogen in this steel increases, so does the proportion of the surface for which brittle transcrystalline growth of the crack is characteristic.

In the case of steel of quality 50CrV4+N, the change in brittleness caused by the action of the hydrogen is not so drastic. Even in the case of relatively high concentrations of hydrogen the hydrogenated steel still retains a certain toughness, which means that in this steel containing alloyed nitrogen other kinds of mechanisms involving the action of hydrogen are present, and this raises the threshold of sensitivity of this steel to hydrogen embrittlement (Figure 2.). The results of the research have shown that, although this type of steel hydrogenates quickly, the presence of nitrogen prevents any drastic worsening in the toughness of the material.

It is known that nitrogen improves numerous characteristics of steels with f.c.c. and, to an even greater extent, with b.c.c. crystal lattices. The effect of nitrogen on toughness, e.g. in the case of austenitic stainless steels, is a particularly brilliant case, since as the yield stress increases so also does toughness, which carbon does not make possible. The increasing of the toughness of highly alloyed tool steels has been a well-known success story, which is connected to the favourable operation of intentionally alloyed nitrogen.

Nitrogen effectively deformationally strengthens the ferritic and austenitic matrix, which, in the case of austenitic stainless steels, is based on the existence of fine Cr-N precipitations and a fine dispersion of nitrogen, which effectively anchor the dislocations. The interaction between the atoms of nitrogen and the dislocations is stronger than that with the atoms of carbon. Nitrogen reduces the stacking fault energy, and as a consequence partial dislocations occur. This means that the stacking fault energy characterizes the thermodynamic stability of the crystal structure and affects the slipping, climbing and shearing of the partial dislocations under the influence of the critical stress which is needed for the initiation and propagation of the crack. The smaller the stacking fault energy is, the greater is the distance between partial dislocations. However, for the movement of partial dislocations, e.g. by climbing or slipping, it is necessary that two partial dislocations are joined into one dislocation. A large stress is needed for such a joining, which is larger the smaller the stacking

fault energy is. Anchored partial dislocations with interstitially dissolved nitrogen require a large additional stress, which enables migration of the dislocations outside the area of the crack tip, and their relaxation. In this way the locally increased strength requires a greater loading, at which further growth of the crack is possible through the area influenced by the nitrogen.

Processes of this kind therefore, in the presence of alloyed nitrogen, increase the toughness of the material. In the given case it can be assumed that the a priori greater

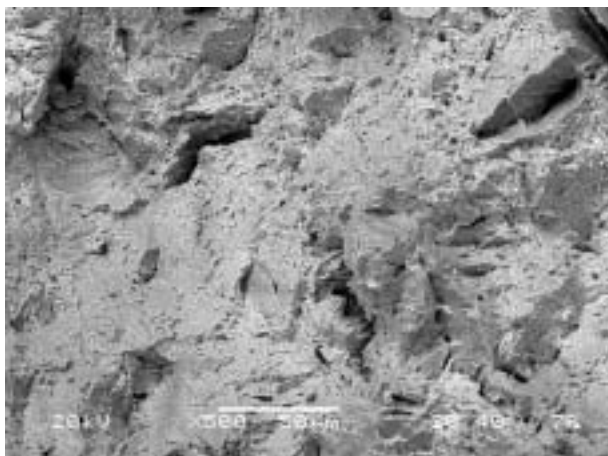


Figure 3. SEM image of the relatively ductile fracture surface of the steel 50CrV4 with a hydrogen concentration of 0.55 ppm
Slika 3. SEM slika krhke prelomne površine čelika 50CrV4 s koncentracijom vodika 0,55 ppm

toughness of the basic non-hydrogenated material is a sufficient condition for the already-mentioned behaviour at the crack tip. As far as hydrogen embrittlement is concerned, it is well-known that metals with a greater ductility (and a greater reduction in area) are more resistant to this phenomenon since they are capable of accumulating a larger part of the released energy, e.g. in the case of the action of hydrogen according to the Zappfe's mechanism (the pressure mechanism). At the same time, propagation of the crack due to the reduction in the binding force between the atoms of the metal (the Troiano-Oriani decohesion mechanism) is slower in the more ductile material. These are the real reasons that, over a wide range of absorbed hydrogen, the threshold of sensitivity to hydrogen embrittlement of the steel 50CrV4+N is much higher. From the results shown in Tables 2. and 3. it can be seen that the hydrogen does not significantly reduce the tensile strength, and it is for this reason that the measurements of reduction in area were introduced, where the negative effects of the hydrogen are most clearly manifested. Depending on the quantity of absorbed hydrogen and on the microstructure with all its constituents, in the case of high-strength steels the yield stress completely disappears (the same is true in the case of the 50CrV4 steel, and in the case of greater

hydrogen concentrations for the steel 50CrV4+N), and the workability of such more or less brittle material is poor. The disappearance of the yield stress is the consequence of the occurrence of brittle areas, where the large internal energy of the system is accumulated. Such an accumulation of brittle areas gradually increases due to the constant regrouping of the mobile atomic hydrogen to more favourable locations, i.e. to traps, and this causes delayed fractures. At a certain static or dynamic loading or during some mechanical manipulation with the material, the brittle regions start to crack. A rapid chain reaction is caused. The consequence of this is the rapid release of accumulated internal energy and coalescence of the remaining brittle areas into a final crack. Since the load-bearing cross-section is reduced below the critical value, the remaining part then fails. The cracking process takes place very quickly, so that the yield stress is not present, or is only weakly expressed. It is quite clear that the workability of such brittle material is poor, and that reworking causes the occurrence of micro and macro cracks. The added nitrogen in the investigated 50CrV4+N steel partially reduces these effects, which means that it slows down the destructive influence of the hydrogen.

The results of fractographic analysis of the fracture surfaces of the hydrogenated test specimens provided, together with the results of mechanical tests and the results

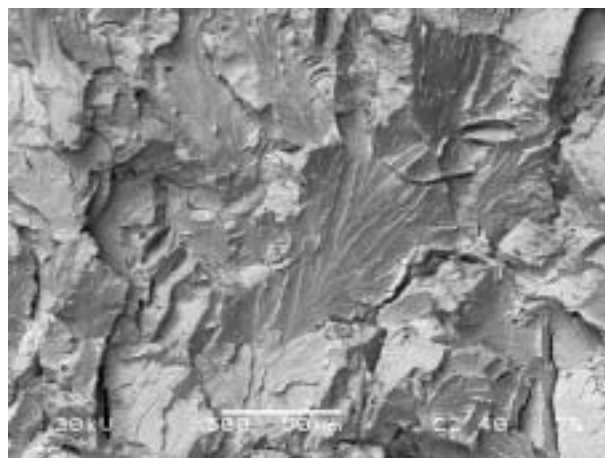


Figure 4. SEM image of the brittle fracture surface of the steel 50CrV4 with a hydrogen concentration of 0.70 ppm
Slika 4. SEM slika krhke prelomne površine čelika 50CrV4 s koncentracijom vodika 0,70 ppm

for reduction in area, a basis for the prediction of the critical quantity of hydrogen in the steel, and such expectations were later proved in practice. It is a fact that reduction in area provides an indirect indication of the toughness of material, and therefore also to some extent of its workability, and the topology of the fracture surface can provide an estimate of the degree of brittleness due to the action of the hydrogen.

The critical quantities of hydrogen are the following:

- in the case of the steel 50CrV4: $H_{crit} \leq 0,60$ ppm,
- in the case of the steel 50CrV4+N: $H_{crit} \leq 0,90$ ppm.

At values lower than the critical value the fracture surfaces are fairly ductile (see Figure 3.), whereas at higher values the proportion of brittle areas rapidly increases. In the case of the steel 50CrV4, complete brittleness occurs already at a hydrogen concentration of 0,7 ppm (Figure 4.). Similar mechanisms manifest themselves in the case of the steel 50CrV4+N, but in this case the threshold of sensitivity is expressed by a higher value of H_{crit} .

CONCLUSIONS

The results of the research have confirmed certain assumptions regarding hydrogen embrittlement, which are based on the theory of traps, on the diffusion of atomic hydrogen into the metal, and its migration within the crystal lattice. The spring steel 50CrV4 is much more sensitive to hydrogen embrittlement than the same steel when alloyed with nitrogen, which has a much higher threshold of sensitivity.

By means of cathodic polarization, which makes possible the controlled hydrogenation of steel, by means of mechanical testing and the determination of the reduction in area of such hydrogenated test specimens, as well as by fractographic analysis of the fracture surfaces, the critical quantity of hydrogen H_{crit} was determined, above which brittle quasi-splitting fractures take place, which are characteristic for hydrogen embrittlement. In the case of the

steel 50CrV4: $H_{crit} \leq 0,60$ ppm, and in the case of the steel 50CrV4+N: $H_{crit} \leq 0,90$ ppm.

In the second part of the research, the parameter H_{crit} was adopted as a basis for the preparation of annealing diagrams for both of the investigated types of steel. In the case of both types of steel, after continuous casting of ingots had taken place a considerable quantity of hydrogen remained in the steel, which resulted in delayed fractures. The annealing diagrams, which define the relationship between the annealing temperature and the quantity of hydrogen in the steel, were prepared on the basis of a physical model of hydrogen diffusion, taking into account appropriate diffusion constants, and the additional computer processing of all these parameters. This work will be presented in a second, companion paper.

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