ROLE OF THE MICROSTRUCTURE IN HYDROGEN INDUCED CRACKING OF CARBON - MANGANESE STEELS

SOJKA J., HYSPECKÁ L.

VŠB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering,

708 33 Ostrava-Poruba, Czech Republic

ÚLOHA MIKROSTRUKTURY PŘI VODÍKEM INDUKOVANÉM PRASKÁNÍ UHLÍK - MANGANOVÝCH OCELÍ

SOJKA J., HYSPECKÁ L.

Vysoká škola báňská - Technická univerzita Ostrava, Fakulta metalurgie a materiálového inženýrství, 708 33 Ostrava - Poruba, Česká republika

ABSTRAKT

Práce hodnotí vztah mezi strukturními charakteristikami C-Mn ocelí používaných v ropném průmyslu a jejich odolností vůči vodíkem indukovanému praskání (HIC). Studované oceli se lišily mikrostrukturou a geometrickými charakteristikami nekovových vměstků. Zkoušení odolnosti vůči HIC bylo prováděno v souladu s předpisem NACE TM 0284. Byl ověřen příznivý vliv jednak kalení a popouštění, ale i "vysokoteplotního" normalizačního žíhání provedeného za teploty 1000°C. U ocelí s feriticko-perlitickou strukturou náchylnost k vodíkem indukovanému praskání vzrůstala s mírou lokálního obohacení řádků perlitu manganem a s rostoucím stupněm řádkovitosti. Vliv sirníků manganu byl méně výrazný.

ABSTRACT

The relations between the microstructure characteristics and the resistance of carbon-manganese steels to hydrogen induced cracking (HIC) were studied for plates used in oil and refinery industry. Steels differed in the non-metallic inclusion characteristics and in the microstructure (heat treatment). Testing of HIC resistance was performed in accordance with NACE TM 0284 standard. As to heat treatment, the beneficial role of quenching and tempering was confirmed but also that of "high" temperature normalising performed at 1000°C. For those steels, microstructure of which consisted predominantly of ferrite and pearlite, the susceptibility to HIC increased with the degree of the local enrichment of pearlitic bands especially in manganese and with the growing degree of banding. The role of manganese sulphides was less pronounced.

Key words: carbon manganese steel, heat treatments, microstructure, pearlitic bands, hydrogen induced cracking

INTRODUCTION

Hydrogen induced cracking (HIC) or stepwise cracking (SWC) is a specific kind of hydrogen provoked damage in carbon and low alloy steels operating in hydrogen sulphide containing environments, especially in steels used for pipelines and pressure vessels in oil and refinery industry. Understanding and controlling the factors that contribute to the observed effects may mitigate this kind of damage. It is generally recognised that resistance of steels to HIC can be correlated with microstructure features [1,2]. The microstructure itself is very important as it is known that resistance to HIC can be considerably improved if quenching and tempering is used, which resulted in martensitic and/or bainitic microstructure [1]. For those steels microstructure of which consists predominantly of ferrite and pearlite there are two favourable sites for HIC - non-metallic inclusions (especially manganese sulphides or stringers of oxides) and the segregation bands containing pearlite or even bainite and martensite. Elongated manganese sulphides are considered as the most dangerous sites [3]. That is why the extremely low sulphur content and calcium treatment of steels are very often required. The most important microstructure parameters that have to be taken into account in HIC are the nature and geometric characteristics of non-metallic inclusions, the local chemical composition of segregation bands and also the degree of the banding [4-7]. The presented paper shows important relations that exist between resistance to HIC and microstructure characteristics of carbon-manganese steels.

EXPERIMENT

Plates of various heats of A516Gr70 steel with the thickness going from 35 to 80 mm were used for experimental studies. The chemical composition of the studied heats is given in Table 1.

Table 1 Chemical composition of A516Gr70 steels (% by mass)

Plates were used after different heat treatments:

Conventional normalising - CN (890°C/air);

Normalising and tempering - NT (890°C/air + 590°C/1.5 hour/air);

High temperature normalising and tempering - HTN (1000°C/air + 590°C/1.5 hour/air);

Quenching and tempering - QT (890°C/water + 590°C/1.5 hour/air).

Testing of the steel resistance to HIC was performed in accordance with NACE TM 0284 standard using specimens oriented in longitudinal direction. After 4-day exposure in the testing solution (NACE TM 0177) cracks were measured on metallographic sections oriented in transversal direction. Additional testing was performed using smooth tensile specimens oriented either in longitudinal or in through-thickness directions of plates. In this case, hydrogen was introduced into the specimens by electrolytical charging. The details of experimental procedure were similar as those described in [4]. Quantitative structure measurements were performed by means of automatic image analysis using Image Pro Plus software.

RESULTS AND DISCUSSION

NACE TESTING

Resistance of steels to HIC was determined by the metallographic measurement of geometric characteristics of the cracks presented on metallographic specimens after exposure in H_2S containing solution. The only parameter shown here is the crack length ratio. This parameter can be described in the following way:

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where **a** represents the length of individual cracks and **w** the specimen width (size parallel to the plate surface).

The crack measurement was performed separately for the surface and for the centre of the plate thickness. Some of the results are given in Table 2.

Table 2 Results of HIC testing - crack length ratio CLR

Role of the Heat Treatment

The results illustrate the fact that all observed cracks were situated in the mid-thickness region of the plates, which reflects the non-homogeneity of the chemical composition and the microstructure. The results also confirm the beneficial role of quenching and tempering to increase HIC resistance [1]. It is in accordance with a generally accepted classification of resistance of different microstructures to hydrogen embrittlement. The resistance of microstructures in increasing order goes from untempered martensite or bainite, through ferrite/pearlite to quenched and tempered bainite and martensite. It must be pointed out that in the presented case resulting microstructure in the mid-thickness of the plate has not been fully quenched and it consisted of tempered bainite and non-negligible amount of ferrite (Fig.1). Nevertheless, even this kind of microstructure was sufficient to increase considerably the HIC resistance and to increase the mechanical properties without any significant degradation of plastic properties and notch toughness.

Another heat treatment has been found that had a positive effect on the HIC resistance. It was a "high" temperature normalising followed by tempering (HTN). The normalising performed at 1000°C resulted in less banded structure of ferrite and pearlite (see Table 3), which could explain the increased resistance to HIC.

Fig.1 Microstructure of A516Gr70 steel after quenching and tempering (mid-thickness)

Table 3 Measurement of the degree of banding

Degree of pearlite banding represents an important parameter, which is often taken into account when speaking about HIC. Very often this relation is expressed only qualitatively showing that the higher is the degree of banding the higher is also the susceptibility of steels to HIC [6]. In the presented study the degree of banding was measured in accordance with ASTM E1268 standard [8], where anisotropy index AI and degree of orientation Ω were calculated, and using the method described by Ryś [9].

The measured parameters are defined as follows:

, ,

where is the number of interceptions per unit length of test lines parallel to the orientation of the pearlitic bands,

is the number of interceptions per unit length of test lines perpendicular to the orientation of the pearlitic bands.

The method described in [9] expresses the degree of banding by means of the following parameter:

, where σ represents the standard deviation of estimation.

Degree of banding is equal to 1 for isotropic structures. The volume fraction was estimated by the lineal analysis with the test lines either parallel or perpendicular to the orientation of the pearlitic bands.

Some of the obtained results are shown in Table 3. Fig.2 shows two examples of the corresponding microstructures.

a) b)

Fig.2 Microstructures of the heat A after conventional (a) and high temperature (b) normalising

It is obvious that relation exists between the degree of banding and the susceptibility to HIC in the central part of the plate thickness. High temperature normalising results in less banded structure which increases the resistance to HIC (CLR parameter decreases). If the degree of banding is calculated in accordance with ASTM E1268 standard the erroneous results are obtained, showing (see Table 3) that the degree of banding is very low and equal for all the microstructures. It is not surprising if we consider that this standard can reveal only that kind of banding where the ferrite-pearlite interface is oriented. Surprising is the fact that nearly all customers ask to measure the degree of banding in accordance with ASTM standard. If the method described in [9] is used correct results are obtained, which enable to classify the degree of banding of different steels (heats).

After HTN the level of mechanical properties corresponded to that obtained after conventional normalising, without any significant degradation. The comparison of mechanical properties of A516 steel after various heat treatments is presented in Table 4.

Table 4 Comparison of the mechanical properties of A516Gr70 steel after various heat treatments

The results shown here demonstrate that quenching and tempering enable to produce steels resistant to HIC with a relatively low carbon equivalent having the mechanical properties corresponding to the higher grades that cannot be obtained after normalising. What is important for the producers is the fact that in case of QT or even in case of HTN the extremely low sulphur content (0,001%) need not be met, thus reducing the production costs. Tempering that followed normalising was beneficial in those cases where non-tempered bainite or even martensite were present in the segregation bands after normalising. It was the case of the heat B (see Table 2).

Ferrite/pearlite Steels

All studied steels were manufactured with a calcium addition. The predominant non-metallic inclusions represented complex oxides containing to various extent mainly Al, Si, Ca, Mg with an outer shell formed by (Ca, Mn)S. Nevertheless, some portion of elongated manganese sulphides was still present. The favourable site for HIC represented especially segregation bands consisting of pearlite and in some cases even of bainite. One example of a typical crack found in steel with microstructure of ferrite/pearlite is shown in Fig.3.

Fig.3 Example of a crack in the steel with microstructure of ferrite/pearlite

The role of manganese sulphides seemed to be less pronounced. Large manganese sulphides that did not initiate any cracks were found in metallographic specimens in the mid-thickness region.

Local analysis of the chemical composition in the segregation bands, performed in the vicinity of the plate surface, in the mid-thickness region (outside the cracks) and directly in the regions where the cracks were present revealed the significant differences in the alloying element content. The obtained results are summarised in Fig.4.

Fig.4 Local chemical composition in segregation (pearlitic) bands - heat A

It is evident that the regions where cracks initiated and propagated were the most enriched mainly in manganese but also in nickel, enrichment in chrome being less important. The higher carbon and phosphorus content can be also expected there but their analysis could not be performed. The results showed that in the presented case the degree of enrichment of segregation bands in alloying elements represented the decisive factor provoking HIC. It is in agreement with some works focused on the properties of steels made by continuous casting technique [7].

It is assumed in some works that susceptibility of steels to HIC can be correlated to the width of pearlitic bands [10]. This possibility was also studied and the obtained results were published elsewhere [2]. In our case, no significant relation could be found between the resistance to HIC and the width of the pearlitic bands. Although the existence of such a relation cannot be denied it seems that it is strongly connected to the local chemical composition of segregation in pearlitic bands. HIC can be found only in those cases where the higher width of the bands is accompanied by their higher enrichment in alloying elements.

Despite of the fact that the role of manganese sulphides or more generally that of non-metallic inclusions is not predominant in the studied case they cannot be completely neglected. A following experiment was performed to verify the role of manganese sulphides in the process of HIC. Small pieces of a plate (heat C) were hot rolled in laboratory conditions so that the initially longitudinal direction became the through-thickness direction and the initially through-thickness direction became the transversal direction. The conventional normalising followed the rolling, using the same conditions as in the initial state. With regard to zhe above described rolling direction, the basic microstructure characteristics, i.e. pearlite content, width of pearlitic bands and the degree of banding, did not changed significantly but the geometric characteristics of manganese sulphides changed. It was found out that the increase of the resistance to HIC after these operations (see table 2) can be correlated with the mean value of MnS area in metallographic sections corresponding to planes parallel to the plate surface (initial and after laboratory rolling). These results are shown in Table 5.

Table 5 Relation between HIC resistance and mean area of manganese sulphides (heat C)

Nevertheless, it must be taken into account that laboratory rolling, which comprised heating at high temperature, could reduce the local peaks in alloying element concentration and thus contributed to more homogeneous chemical composition. This possibility will have to be verified.

TENSILE TESTING

Additional hydrogen embrittlement tests performed on previously hydrogen charged tensile specimens showed a strong anisotropy of mechanical properties but only in the presence of hydrogen. The presence of hydrogen manifested itself in a drop of plastic properties expressed by the reduction in area (RA), especially in the through-thickness direction. Fracture surfaces were entirely brittle for this orientation while in longitudinal direction the fracture surfaces consisted of a mixture of transgranular brittle and ductile fracture. Cracks provoked by hydrogen initiated on the stringers of manganese sulphides. In this case, the most important sites for HE represented non-metallic inclusions. It differed from the material behaviour in NACE tests. It could be the result of the simultaneous role of hydrogen and applied stress and accompanied bulk plastic deformation during tensile tests. It was found out that the drop of reduction in area could be correlated with the mean value of the area of MnS inclusions in the section planes perpendicular to the specimen axis and with the width of the pearlitic bands on the same planes. Some of the results are presented in Fig.5, fracture surface typical for the through-thickness direction is demonstrated in Fig.6.

Fig.5 Relation between mechanical properties (RA) and microstructure characteristics for the different orientations of the tensile specimens

Fig.6 Fracture surface of a tensile specimen tested after hydrogen charging (through-thickness direction)

CONCLUSIONS

The study of resistance of carbon-manganese steels to hydrogen induced cracking showed its close relation to microstructure characteristics. Quenching and tempering but also high temperature normalising performed at 1000°C followed by tempering increased considerably the resistance to HIC. Satisfactory results were obtained even if sulphur content slightly exceeded the recommended limit. No significant degradation of mechanical properties was observed. On the contrary, in case of quenching and tempering the mechanical properties were higher in comparison with the conventional heat treatment. For those steels, which had microstructure consisting of ferrite and pearlite, the decisive factor provoking HIC seemed to be the local enrichment of segregation bands in alloying elements. The role of manganese sulphides, although present in the microstructure, was less important. Tensile testing on previously hydrogen charged specimens revealed a strong anisotropy of mechanical properties. In this case, cracks were initiated predominantly on manganese sulphides. The observed anisotropy could be correlated to the geometric characteristics of non-metallic inclusions and pearlitic bands.

ACKNOWLEDGEMENT

The results of the project LN00B029 were supplied with subvention by The Ministry of Education of Czech Republic.

Literature

[1] Coudreuse, L., Zmudzinski, P., Bocquet, P., In: Proc. Sec. Int. Conf. On Interactions of Steels with Hydrogen, Wien, Austria, (1994), p.401

[2] Sojka, J. et al.; In :Proc. of STERMAT2000, Krakow, Poland,September (2000), p.391

[3] Wilson, A.D., In: Proc. Of the Symp. On Advances in the Production and Use Steel with Improved Internal Cleanliness, Atlanta, USA, (1998), p.73

[4] Sojka J.: Evaluation of Hydrogen Embrittlement of Steels Used as Storage Tanks in Chemical Industry (in Czech). Tech. report Vítkovice, a.s., (1997), p. 1 -25

[5] Timmins P.: Solutions to Hydrogen Attack in Steels. American Society for Metals, Metals Park, OH, (1997), p.107-111

[6] Kane, R., Cayard, M. S., Prager M.: Evaluation of Advanced Plate Steels for Resistance to HIC and SOHIC in Wet H_2S Environments. Proc. Sec. Int. Conf. on Interaction of Steel with Hydrogen in Petroleum Industry in Pipeline Service, Wien, (1994), p. 31

[7] Murakami, K. et al.: JISI of Japan, Vol. 85, (1999), p.301

[8] ASTM Standard Practice for Assessing the Degree of Banding or Orientation of Microstructures. Annual Book of ASTM Standards, Vol.03.01, (1991), p. 890

[9] Ryś J.: Stereologia materiałów. Fotobit-Design, Kraków, (1995), p.275

[10] Mazur A.: Materials Performance, (1995), p. 52