1. Introduction

Supermartensitic steels represent an important group of steels used at present in ever growing extent particularly in oil and gas industries, where they are offered as an attractive alternative for submarine pipelines [1-3]. Supermartensitic steels are characterised by high strength and toughness, resistance to corrosion in CO2 environment with low contents of H2S and weldability without pre-heating. No annealing for stress reduction is made after the welding [4, 5].

Supermartensitic steels are also characterised by low content of carbon (below 0.015 wt. %), content of chromium 11 – 13 wt. % ensuring resistance to corrosion, content of nickel 5.5 – 6.5 wt. % ensuring perfect austenitisation and transformation to martensitic structure after cooling, and content of molybdenum 2 – 2.5 wt. % ensuring resistance to local types of corrosion and increased resistance to SSC (sulfide stress cracking). Apart from the above mentioned main alloying elements some other elements are also used, such as copper, titanium and vanadium, which serve for optimisation of martensitic structure without occurrence of δ-ferrite, for enhancement of resistance to corrosion or as technological additions, e.g. for grain refinement. These steels have always very low content of sulphur, max. 0.003 wt. %. Total chemical composition is balanced in such a manner that it would be possible to obtain by appropriate heat treatment a martensitic structure with certain portion of reverse austenite γ_{rev.} [5].

2. Experimental material

Supermartensitic steel 13Cr6Ni2.5Mo was used for experiments. Its chemical composition is given in the Table 1.

| TABLE 1 |
|-------------------|
| Chemical composition of supermartensitic steel, wt. % |
| C           | Cr           | Ni          | Mo         | Mn        | Si         | V         |
| 0.0124      | 12.53        | 6.33        | 2.33       | 0.51      | 0.26       | 0.028     |
| P           | S            | Al          | Cu         | Ti        | N          |
| 0.014       | 0.003        | 0.042       | 0.086      | 0.13      | 0.01       |

Due to reduction of strength characteristics the steel was subjected to heat treatment (HT) by the mode 970 °C/1 h/air + 580 °C/6 h/air + 580 °C/6 h/air. Content of retained austenite in microstructure was approx. 11 wt. %. Basic mechanical properties were determined on universal tension testing machine 100 kN and their values are given in the Table 2.

| TABLE 2 |
|-------------------|
| Basic mechanical properties of supermartensitic steel (longitudinal direction) |
| Type of specimen | R_{p0.2}, MPa | R_{m}, MPa | R_{p0.2}/R_{m} | A_{5} % |
| Basic material   | 885           | 967        | 0.92           | 20     |
| Welded joint (WJ)| 782           | 942        | 0.83           | 7.5    |

Structural analysis of the samples was made with use of light microscope ZEISS NEOPHOT 32. Unfortunately certain areas of martensitic structure in basic material contained δ-ferrite, which degrades properties of supermartensitic steels. Microstructure of basic material is shown in the Fig 1. Microstructure of the welded joint is shown in the Fig. 2. Weld metal (WM) has a coarse-grained martensitic structure. Heat affected zone (HAZ) has fine grained martensitic structure without coarse grained area at the fusion line.
3. Experimental procedure and results of SSC tests

Testing was made in full compliance with the directive NACE TM 0177-03. Method A was used, testing solution B with higher pH value. Results are summarised in the Fig. 3 a, b.

It is obvious from the Fig. 3 a, b that all the testing samples were fractured and in a very short time interval. It is therefore possible to state that the samples were under the given testing conditions insufficiently resistant to SSC. An example of cracking in the basic material, which was probably caused by superposing effect of hydrogen induced cracking (HIC) and SSC is shown in the Fig. 4.

Fracture areas of samples were subjected to fracture analysis on scanning electron microscope JSM 6490. Overall appearance of fracture areas was similar both in basic material and in welded joint. It was always possible to discern the area of slow propagation of crack and area of final rupture, see the Figs 5 and 7.

Fracture areas of basic material had zones with different morphology. Characteristic photos are shown in the Fig. 6 a, b, c.

Fracture areas of the welded joint were characterised by the zones of transgranular brittle fracture Fig. 8 a, b and some areas of ductile fracture with characteristic dimple morphology were observed as well Fig. 8c.
4. Conclusion

The work was focused on evaluation of resistance of the welded joint made of supermartensitic steel 13Cr6Ni2.5Mo to SSC. Resistance of the welded joint and also of the basic material to this type of failure was insufficient. This fact can be attributed to high values of mechanical properties of material, which did not sufficiently decrease by tempering, and also to occurrence of undesirable δ-ferrite in structure. In spite of that it was revealed that the welded joint brought even further reduction of resistance to SSC, because the fracture occurred in the samples with welded joint primarily in the weld metal (WM) or in heat affected zone (HAZ) and not in the basic material. More experiments aimed at confirmation of this trend will be made with samples loaded by lower values of tension.

Acknowledgements

This report has been prepared in frame of the project TAČR TA03010161 and the Project No. LO1203 „Regional Materials Science and Technology Centre-Feasibility Program“ funded by Ministry of Education Youth and Sports of the Czech Republic.

REFERENCES

[1] K. Kondo, M. Ueda, K. Ogawa, H. Amaya, H. Hirata, H. Takabe, Proceedings of Supermartensitic Stainless Steels, 11–18 (1999).
[2] A. Dhooge, Stainless Steels World, 52-55 (1999).
[3] M. Kimura, Y. Miyata, Y. Yamane, T. Toyooka, Y. Nakano, CORROSION‘97, NACE, 22 (1997).
[4] D. Carrouge, P. Woollin, Proceedings of Stainless Steel World, 61-67 (2002).
[5] P. Woollin, A. Kostrivas, Proceedings of OMAE, 92351 (2006).
[6] Y. Miyata, M. Kimura, H. Nakamichi, K. Sato, N. Itakura, K. Masamura, Proceedings of International Corrosion Conference EUROCORR, Nice, France ISBN 2-901785-82-4, CD-ROM (2004).
[7] J. Bilík, P. Pustějovská, S. Brožová, S. Jursová, Scientia Iranica 20, 2, 337-342 (2012).
[8] P. Pustějovská, S. Jursová, S. Brožová, Journal of the Chemical Society of Pakistan 35, 3, 565-569 (2013).
[9] P. Pustějovská, S. Brožová, S. Jursová, Metal Conference Proceedings 79-83 (2010).
[10] A. Konstanciak, S. Brožová, P. Pustějovská, Rynek Energii 107, 4, 33-36 (2013).
