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HYDROGEN EMBRITTLEMENT OF WELDED JOINT MADE OF SUPERMARTENSITIC STAINLESS STEEL IN ENVIRONMENT CONTAINING SULFANE

The work is focused on evaluation of resistance of the welded joint made of supermartensitic 13Cr6Ni2.5Mo stainless steel to sulfide stress cracking. Testing method A and solution B in accordance with NACE TM 0177 were used. All the testing samples were ruptured in a very short time interval but welded joint samples were fractured primarily in the weld metal or in heat affected zone and not in the basic material. Material analysis of samples were made with use of a ZEISS NEOPHOT 32 light microscope and a JEOL 6490LV scanning electron microscope.

Keywords: hydrogen embrittlement, sulfane, tensile test, supermartensitic stainless steel, weld joint

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.

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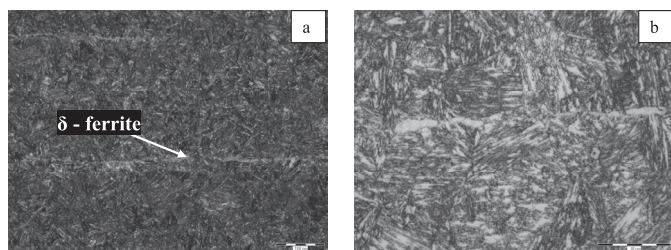


Fig. 1. Microstructure of basic material

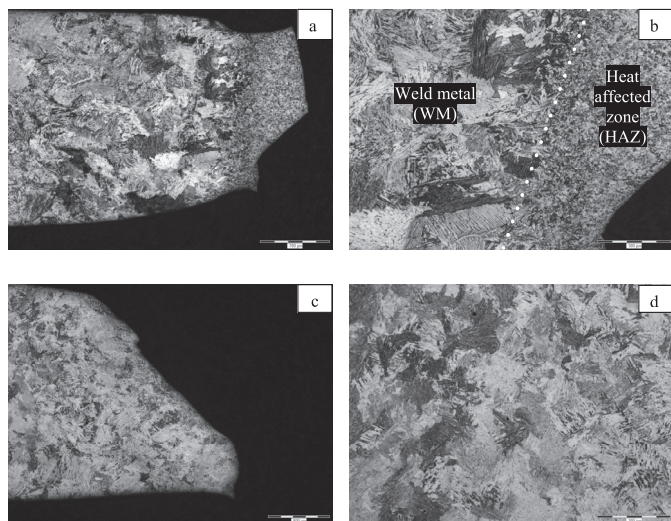


Fig. 2. Microstructure of welded joint

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.

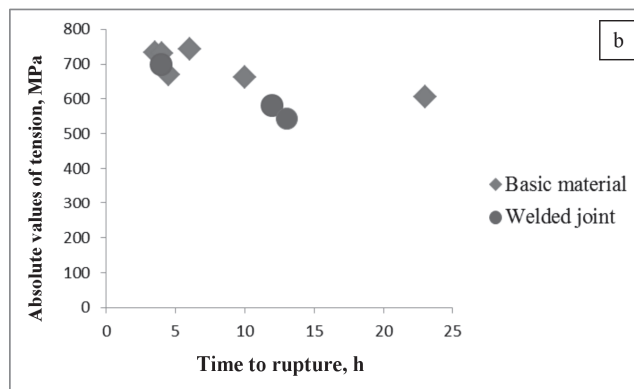
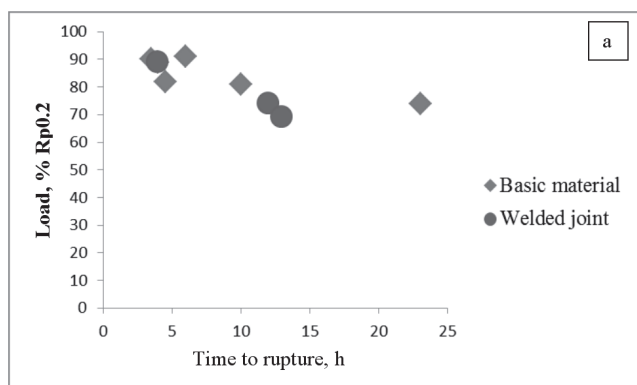


Fig. 3 Results of SSC tests

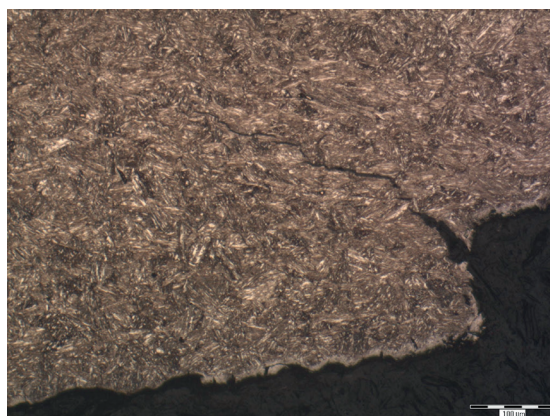


Fig. 4. Example of cracking in basic material (superposition of HIC and SSC)

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.

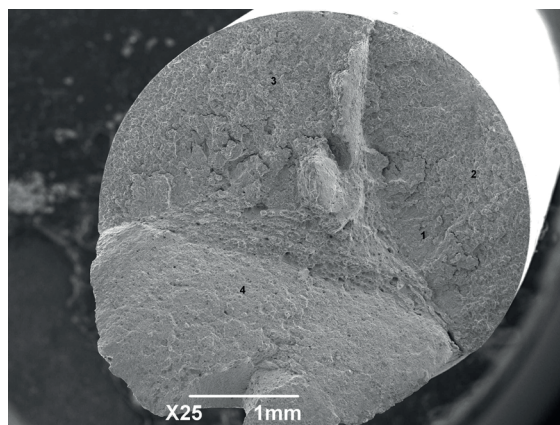


Fig. 5. Overall appearance of the fracture area of basic material, load 82 % R_{p0.2}, time to rupture 4.4 h

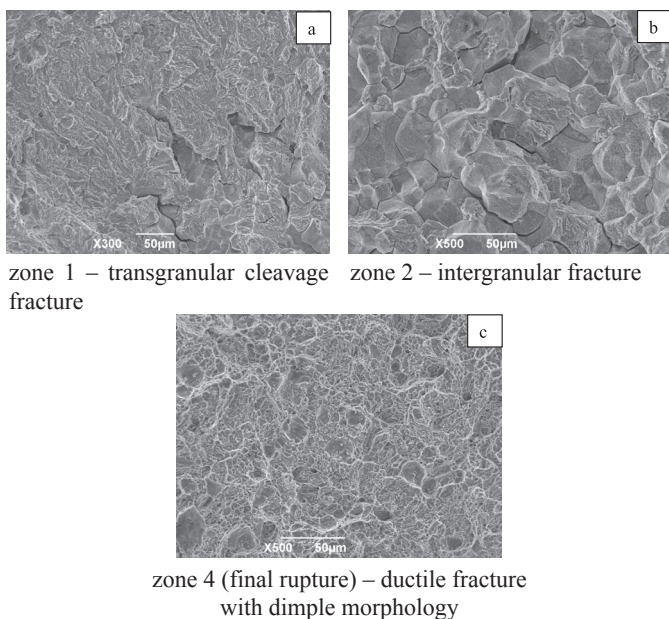


Fig. 6. Fracture – basic material, load 82 % $R_{p0.2}$, time to rupture 4.4 h

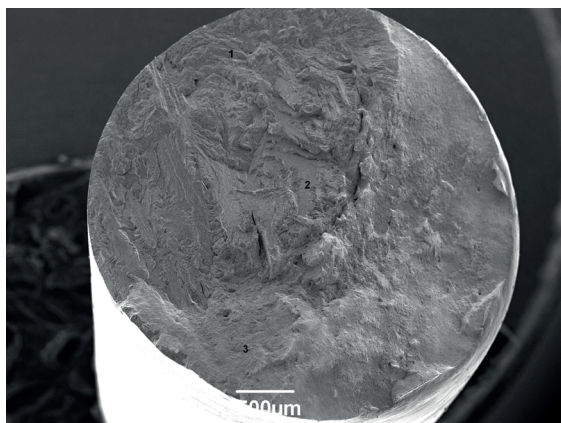


Fig. 7. Overall appearance of the fracture area of welded joint, load 74 % $R_{p0.2}$, time to rupture 12.10 h

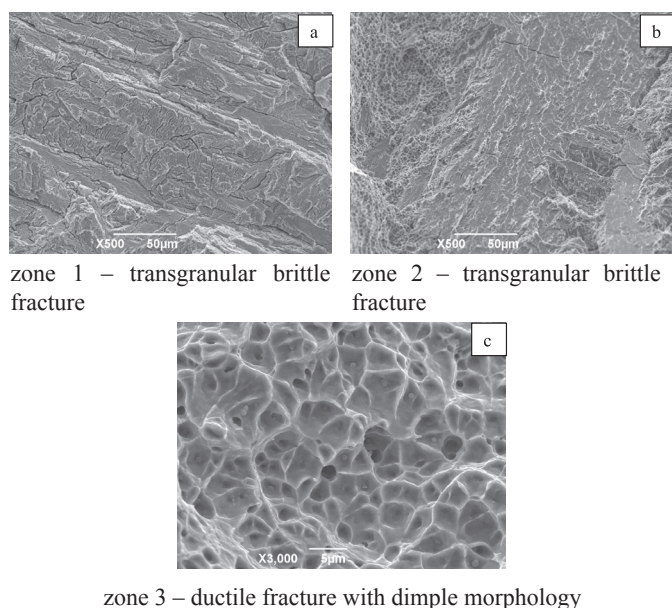


Fig. 8. Fracture area - welded joint, load 74 % $R_{p0.2}$, time to rupture 12.10 h

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

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