SUSCEPTIBILITY OF 304 SS-Ti BIMETAL
TO HYDROGEN INDUCED CRACKING

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ABSTRACT
The work deals with evaluation of hydrogen induced cracking of 304 SS-Ti bimetal after explosive bonding. Both joined materials individually show a good resistance against hydrogen embrittlement. For bonded materials sinusoidal interface with curls is typical. In curls and in their vicinity intermetallic phases are often detected. Those represent hard and simultaneously more brittle areas which can be sensitive to hydrogen induced cracking. The bonding line can be also a potential position for hydrogen concentration. After welding and exposition in corrosion solution bubbled with sulphide hydrogen the Ti of commercial purity and stainless steel 304 SS showed numerous thin cracks detected right in the intermetallic phases. The total crack sensitivity ratio (CSR), crack length ratio (CLR) and crack thickness ratio (CTR) were evaluated according the NACE Standard TM0284 item No. 21215. The results were confronted with the Specification 5L ANSI/API valid for OCTG. The work also includes chosen parameters (e.g. wave length, amplitude, intermetallic particle evaluation etc.).
Keywords: 304 SS-Ti bimetal, intermetallic phase, hydrogen induced cracking

1. INTRODUCTION

Bimetal of 304 SS-Ti type consists of two resistant materials against hydrogen cracking. Generally, the austenite steel does not show evidence of hydrogen-induced lattice de-cohesion and, thus, degradation will occur only through a hydrogen-dislocation interaction or by internal pressure formation. Hydrogen has a greater solubility in the FCC lattice than in the BCC one. Hydrogen transport by lattice diffusion is several orders of magnitude less rapid, making hydrogen movement far more difficult. The stabile austenitic steels that generally show high stacking fault energy (SFE) and/or readily cross-slip will exhibit a fairly uniform movement of hydrogen into the steel and minimum of degradation in comparison with materials that have low SFE or for some other reason exhibit planar slip will concentrate the hydrogen along the slip plane [1]. Obstacle existence in form of inclusions precipitates or grain boundaries within the slip planes influence the hydrogen trapping. Under that condition hydrogen can be stripped from dislocation and create localised hydrogen concentrations [2]. The HCP Tiα-phase can retain significant hydrogen in solid solution at elevated temperatures. With lower temperature the hydrogen solubility in mentioned material markedly decreases. At ambient temperature it is 10^{-3} at. % [2]. The excess hydrogen is precipitated as a metal hydride. The formation of the hydrides must involve the movement of both the titanium atoms and hydrogen and, consequently, the habit planes and orientation relationships of the hydrides are in relation tend to dislocation modes of transformations. When a hydride is formed in the Tiα, there is about 18% volume increase. The volume increase must be accommodated by the host lattice and it results in sizable elastic and plastic strains. These strains can increase the effective solubility of hydrogen in the

host lattice by making nucleation of the hydride more difficult. Hydrogen solubility has been observed to increase in Tiα with increasing yield strength, since this increase in elastic strain energy and plastic work must be supplied by a greater chemical potential or hydrogen super-saturation [2]. Hydrogen transport by lattice diffusion is slow in Tiα and slightly greater than in the FCC iron. According the work [4] the diffusion rate at 200°C is of about 5.10^{-13} $m^2.s^{-1}$. The transport of hydrogen into Tiα from external environment is made even more difficult by the hindering influences of the possible surface films, either oxides or hydrides [2, 4]. After bonding interface of both welded materials shows sinusoidal form with curls. In these curls and their vicinity intermetallic phases can be often detected. The intermetallic phases are mostly on the basis of Ti, Fe, Cr, Ni and some other balanced elements [5]. As each intermetallic the revealed types in the curls of the 304 SS and Ti interface are characterised by higher strength and lower plasticity. This fact may contribute to higher susceptibility to hydrogen embrittlement. Of course, the forms of intermetallics, their represented proportion and distribution influence the hydrogen concentration level. The bonding line could be also a potential position for hydrogen concentration especially in case of coarser and/or localised oxides presence as it was reported in works [6, 7]. In the sandwich interface Berdychenko [6] detected various Ti oxygen types (TiO, Ti_3O and Ti_2O_3) after explosive welding of Ti and C-Mn steel. According the work [6] those inclusions are formed during welding process before the own bonding. Oxygen and also nitrogen get to Ti surface from air and are part of compressed gases formed during welding at high temperatures. It results in decrease of hardness and strength of the titanium. Ghosh [7] revealed very low volume fraction of Fe_2Ti_4O after diffusion bonding of Ti and C-Mn steel. Other oxide types were not observed by him.

Above given intermetallic phases could be very strong localised traps (positions) for hydrogen trapping and leading to dangerous hydrogen embrittlement. To hydrogen induced cracking of bimetal 304 SS-Ti has not been paid too attention by now. Consequently, it is aim of presented work.

2. EXPERIMENTAL APPROACH

For investigation of hydrogen induced cracking stainless steel 304 SS and Ti of commercial purity explosively welded (in EXPLOMET Opole) was used. The bimetal sheet corresponded to 110 mm (304 SS) and 6 mm (Ti). The chemical composition of Ti was followed (in wt. %): 0.01C, 0.05Fe, 0.05O, 0.005N, 0.006H and chemical composition of 304 SS corresponded to (in wt. %): 0.04C, 0.45Si, 1.95Mn, 18.42Cr, 9.74Ni, 0.0065P and 0.011S. At ambient temperature using the TMS machine tensile tests of bimetal were carried out according standard ČSN EN ISO 6892-1. From bimetal three samples of dimensions 20 x 14.5 x 100 mm were manufactured which were exposed in corrosion solution during 96 hours [8]. In the beginning of the test the pH corresponded to 2.66 and the final pH was 3.96. The test temperature reached 25±3°C. Critical parameters of the hydrogen induced cracking the CLR (crack length ration), the CTR (crack thickness ratio) and the CSR (total crack sensitivity) were mathematically evaluated according the NACE Standard [8]. The corrosion test and own evaluation were in agreement with NACE Standard TM 0284 item No. 21215 and the results were confronted with ANSI/API specification 5L [8] generally used for oil country tubular goods. According the mentioned specification the parameters CLR, CTR and CSR should be equal and/or lower than 15 %, 5 % and 2 % (introduced in sequence). Each of three exposed samples was divided into four same perpendicular sections. Consequently, nine samples were prepared for the metallographic evaluation, again in agreement with the NACE Standard [8]. The bimetal was etched in nitric acid and hydrofluoric acid and in water solution of hydrochloride and nitric acid. Metallographic evaluation of cracks was carried out using the light microscope OLYMPUS X70 and the electron microscope SEM JEOL LSM-6490 equipped with EDAX.

3. RESULTS AND DISCUSSION

After explosive welding the bimetal tensile test showed followed parameters: yield stress and strength (YS, TS) corresponded to 410 MPa and 561 MPa, while the ductility (A_5) was on the level of 38 %. The reached YS and A_5 are by 230 MPa and 17 % higher than the minimal specified levels and the reached down and upper reserves of strength show 101 MPa and 119 MPa in comparison with the required values for the 304 SS-Ti bimetal. After exposition of bimetal samples in corrosion solution

with bubbled hydrogen sulphide the metallographic investigation revealed numerous thick and shorter cracks in intermetallic phases as was already reported formerly [5]. The cracks length was lying in interval 0.01-0.08 mm, the thickness was min. 0.01 mm and max. 0.22 mm. The maximal values of the cracks dimensions were detected seldom. The total number of all revealed cracks corresponded to 84. None cracks were observed outside intermetallic phases. On the basis of detected cracks and their dimensions the Table 1 summarises results of calculated hydrogen induced cracking parameters.

Table 1. Found hydrogen induced cracking parameters of
304 SS-Ti bimetal

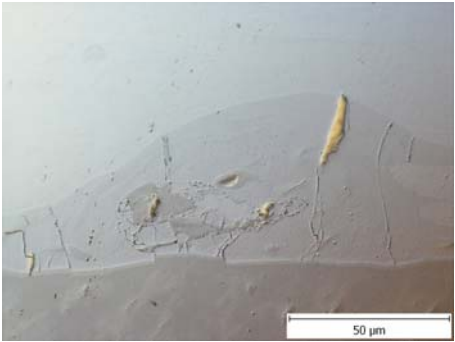| Sample	CLR	CTR	CSR	CLR	CTR	CSR
	individual measurements			mean values of three samples		
	[%]					
1	1.04	2.47	0.003	1.44	2.44	0.04
2	1.25	2.25	0.01			
3	2.04	1.99	0.01			
4	3.07	2.17	0.01	3.55	2.95	0.01
5	3.42	2.93	0.01			
6	4.15	3.75	0.01			
7	2.25	2.30	0.01	2.39	2.24	0.01
8	1.92	1.90	0.01			
9	3.02	2.51	0.01			

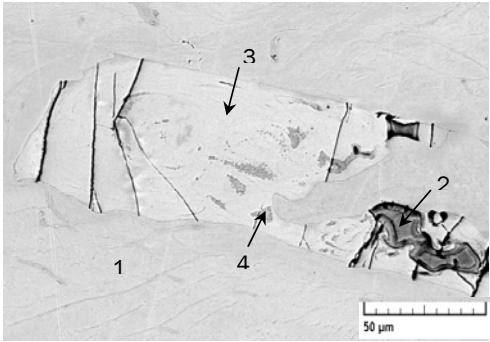*Figure 1. Bimetal interphase with intermetallic phases*

Figure 2. Wave of bimetal interphase with intermetallic phases (description in text)

As the results in Table 1 demonstrate, all parameters are satisfactory and comply with the requirements of the ANSI/API specification 5L. The worst individual CLR parameter showed 10.85 % reserve (sample 6), while in the best case (sample 1) it was 13.46 %. Regarding the CTR parameter the minimal reserve corresponded to 1.25 % (again sample 6) and the maximal one to 3.10 % (sample 8). The total CSR parameters are approximately on the same level and are minimally by 1.99 % under the permissible value. After exposition in corrosion solution, the chosen microstructure of the bimetal 304 SS-Ti Fig. 1 shows. The cracks were only localised in intermetallic phases. Propagation of cracks into basic material (304 SS) or to cladded material (Ti) was not revealed as it also Fig. 2 demonstrates. This one represents microstructure of one area with intermetallic phases after exposition, as well. The point 1 represents material 304 SS, the 2 is Ti matrix, in 3 was analysed (in at. %) 16 Ti, 16 Cr, 57

Fe, 8 Ni and Al, Si, Mn balanced while in area of 4 about 20 Ti, 11Cr, 61 Fe, 6 Ni and Al, or Si and/or Mn balanced was found.

No cracks and cavities were observed in material before exposition in corrosion solution which could be good potential areas for hydrogen catching and thereby for possible better hydrogen conditions of the tested material. In such free spaces a lot of hydrogen could be lost without negative influence on the bimetal. In detail the analysis of bonding line and area of curls in its vicinity was presented recently [5]. On the contrary, a lot of deformation bands and ultrafine grains of both microstructures in the vicinity of the interface as a consequence of strong deformation caused by explosive welding represent numerous potential positions for more uniform hydrogen redistribution and so the better conditions for the more favourable hydrogen resistance. Oxides were also not detected in the bimetal interface as was presented in work [5]. On one side, oxides as well as other particles in matrixes generally could also influence higher material resistance against hydrogen embrittlement as potential hydrogen traps, on other side mentioned particles could degrade the bimetal properties, especially when those would be observed in the bonding line or in its close neighbourhood in localised form. Any in-homogeneity represents higher dangerous of hydrogen susceptibility.

4. CONCLUSIONS

Hydrogen induced cracking of 304 SS-Ti bimetal of commercial purity explosively welded was investigated. The evaluation was carried out by use of the same technique as it is usual in case of oil country tubular goods.

All cracks were only detected in intermetallic phases, first of all in the most frequent type showing about 16-20 Ti, 15-16 Cr, 53-57 Fe, 8 Ni with balanced Al, Si, Mn (in at. %). Those were observed in the vicinity of the 304 SS and Ti interface, mostly in curls of the sinusoidal bonding line and their evaluation was presented in previous work in detail [5]. No cracks and cavities were revealed in the bimetal interface or in its neighbourhood as well as inclusions which could significantly influence the hydrogen response. The cracks in intermetallic phases did not initiated crack propagation to basic materials. Even when the crack number was relatively high (84), their length and thickness did not exceeded 0.08 mm and 0.22 mm (in sequence). These extreme dimensions were detected in few cases only. On average the cracks dimensions were in hundredths of mm.

5. ACKNOWLEDGEMENT

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