

K. Lublińska¹, O. Tsyurulnyk², M. Hredil², H. Nykyforchyn², K.J. Kurzydłowski¹

¹Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141, 02-507 Warsaw, Poland

²Karpenko Physico-Mechanical Institute NASU, Departure of Corrosion-Hydrogen Degradation and Material Protection, Lviv, Ukraine

STRESS CORROSION CRACKING OF THE CLAD STRUCTURAL STEEL AFTER ITS HIGH TEMPERATURE HYDROGEN DEGRADATION

ABSTRACT

It is known that long term service of installations in energy and refinery industry in conditions of simultaneous action of loading and corrosion-hydrogen environments causes degradation of structural steels. This process of degradation is the most intensive on grain boundaries. Therefore structures with clad metal, namely, refinery shell, should be especially sensitive to degradation process. Three types of clad metal “low alloy steel/stainless steel” were studied: 15HM/304L, 516GR60/410S and 516GR70/N201. In-service degradation was modeled by thermocycling of specimens in the range of 25-550 °C in hydrogen atmosphere with fast rate of cooling. It allows to fix at low temperature such amount hydrogen in metal which is in equilibrium at high temperature and this is the reason of the intensive hydrogen degradation. Metal was tested after 30 and 100 thermocycles. Sensitiveness to hydrogen degradation was evaluated by slow strain rate tension of specimens during moderate cathodic polarisation. Some peculiarities of hydrogen cracking of clad metal were established and it was revealed that thermocycling in hydrogen atmosphere increases sensitivity of clad metals to hydrogen degradation. The degradation level depends on the type of clad metal and number of thermocycling.

Key words: thermocycling, clad metal, cracking, hydrogen degradation

INTRODUCTION

One of the important units of refinery is reactor shell which is subjected to the corrosion-hydrogen effect of technological environment at high pressure and temperature [1, 2]. Cladding by stainless steel is used for corrosion protection of a low-alloyed steel of a shell. However one should assume hydrogenation of metal in spite of an existence of the protective cladding layer. On the other hand thermal cycling of a shell metal during shutdowns intensifies hydrogen concentration just in the local volumes closed to interface between two different metals. It is caused by a great difference in a solubility and diffusion rate of hydrogen in ferritic and austenitic steels [1]. Additionally thermal cycling in gaseous hydrogen from working to ambient temperature provides microstructural changes which can cause a decrease of plasticity and crack growth resistance [2].

The aim his work was– to study the effect of thermal cycling in gaseous hydrogen on mechanical behaviour and hydrogen embrittlement of some types of stainless cladding low-alloyed steels with stainless cladding performed by the explosive method.

EXPERIMENTAL

Three composites of low-alloyed (or carbon) steel – stainless steel (or Ni) were investigated: I – the parent A-516 Gr.60 steel was cladded with 410S ferritic stainless steel (flyer); II – 13CrMo4-5 (15HM) steel was cladded with 304L austenitic stainless steel; III - SA-516 Gr.67 steel was cladded with Ni (SB-162 N02201).

Specimens with rectangle section of working part were oriented along the bonding boundary (Fig. 1). These specimens were cut from the bars 12x18x180 mm which formerly were thermocycled (30 and 100 cycles) in hydrogen chamber. The thermocycling procedure is described elsewhere [3]. The conditions were following: heating from ambient temperature to 550°C, with the temperature rate increase of 2÷3 °C/s, holding at this temperature for 30 min and then cooling with the temperature rate of 2÷3 °C/s with following holding at ambient temperature for about 30 min. The mechanical properties and susceptibility to hydrogen embrittlement of composites were investigated by slow strain rate tension (SSRT) method with strain rate of 10^{-6} s^{-1} .

During loading the samples were hydrogen charged with current density of 1 mA/cm^2 . Water solution of H_2SO_4 (pH4) with addition of thiourea (2g/dm^3), which is both corrosion inhibitor and stimulating agent of hydrogen charging, was used.

Diagrams “stress σ – elongation Δ ” were registered by the load and strain gauges, which were located out of the chamber.

Fractography investigations of the fracture surfaces after the tests were carried out using scanning electron microscopy (SEM) HITACHI S-2600N.

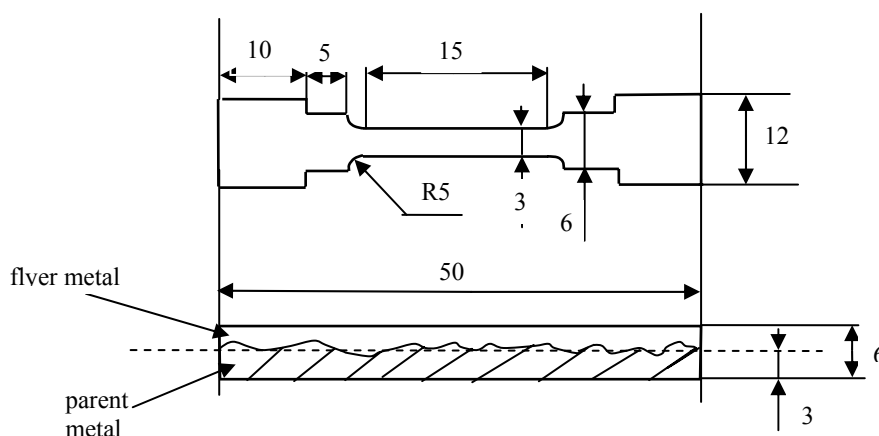


Fig. 1. Geometry of the specimen, dimensions in mm

RESULTS AND DISCUSSION

The stress-strain curves “ $\sigma - \Delta$ ” are presented in the Fig. 2.

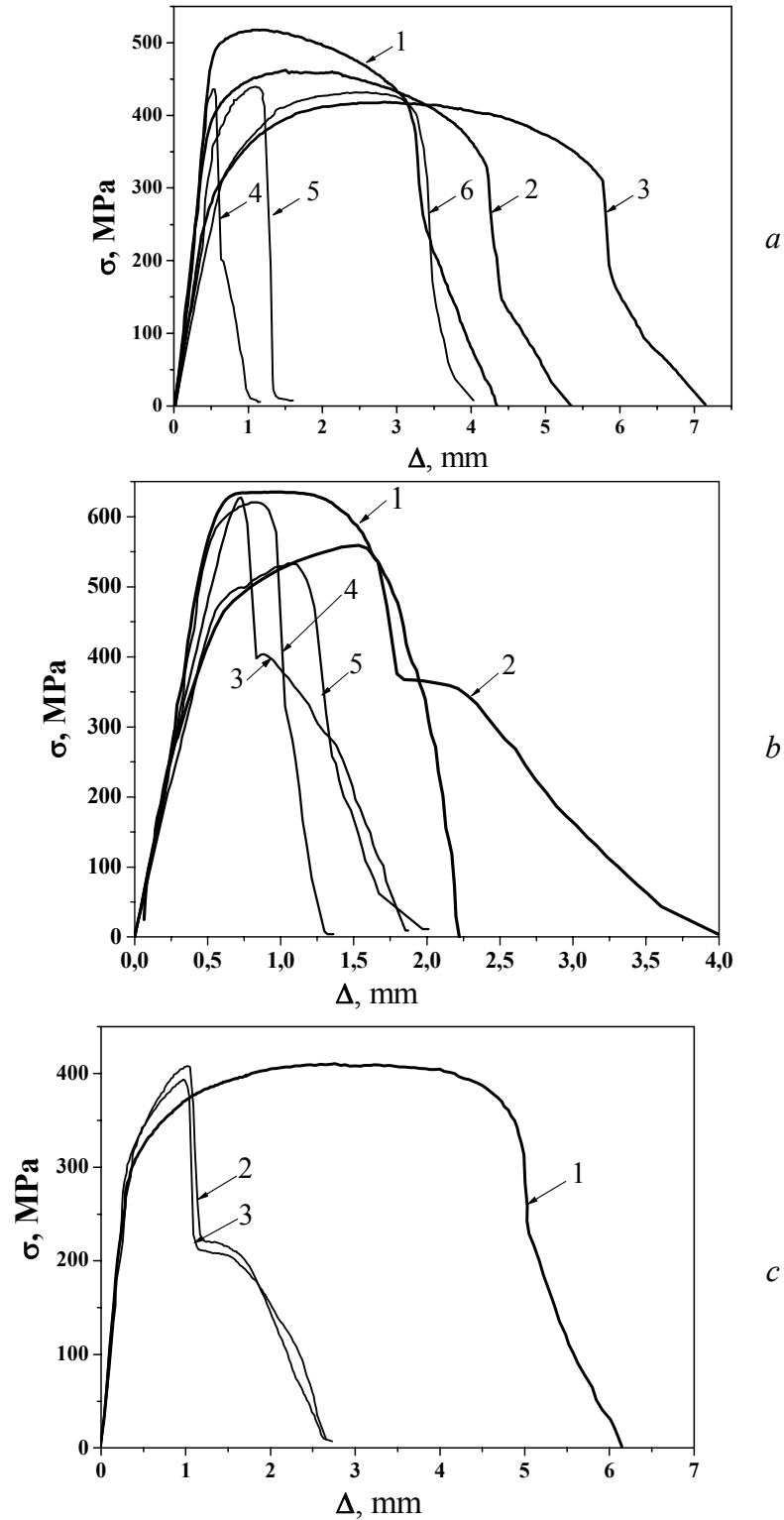


Fig. 2. Curves “ $\sigma - \Delta$ ” for the composites I (a), II (b) and III (c): a – 1,4 – initial state; 2,5 – 30 TC; 3,6 – 100 TC; 1,3,2 – air; 5,4,6 – hydrogen charging; b – 1,3 – initial state; 4 – 30 TC; 2,5 – 100 TC; 1,2 – air; 3,4,5 – hydrogen charging; c – 1 – initial state, air; 2 – initial state, hydrogen charging; 3 – 30 TC; hydrogen charging

As can be seen the studied materials in initial state in air are ductile. On the other hand the stress-strain curves for the all hydrogenated composites show substantial reduction of elongation with the following rapid fracture. For the composites I and II the initiated brittle crack grows with high rate up to critical size but for the more ductile composition III crack grows more slowly.

The mechanical properties of the investigated composites are given in Table 1. As can be seen the ultimate tensile strength and yield strength are risen in a sequence III < I < II.

Table 1. The mechanical properties in air of studied composites

Composite	Material	Initial			30 TC		100 TC	
		$\sigma_{0,2}$	σ_B	HRB	$\sigma_{0,2}$	σ_B	$\sigma_{0,2}$	σ_B
I	Carbon steel	460	520	86	380	465	255	420
	410S			82				
II	Low-alloyed steel	560	635	89			300	560
	304L			100				
III	Carbon steel	320	415	81				
	Ni			58				

The difference in the mechanical properties obviously is caused by the properties of the flyers (Ni and stainless steel). Hardness of the all parent metals is in the range of 81...89 HRB, while HRB for Ni and flyer stainless steels is risen similarly to their strength: III < I < II. This is one of the reasons which explains different properties of hydrogenated composites.

SEM observations of fracture surfaces showed a ductile fracture for both parts of composites in initial state in air and without cathodic hydrogen charging (Fig. 3 *a, b*) but the most ductile fracture was observed for composite III.

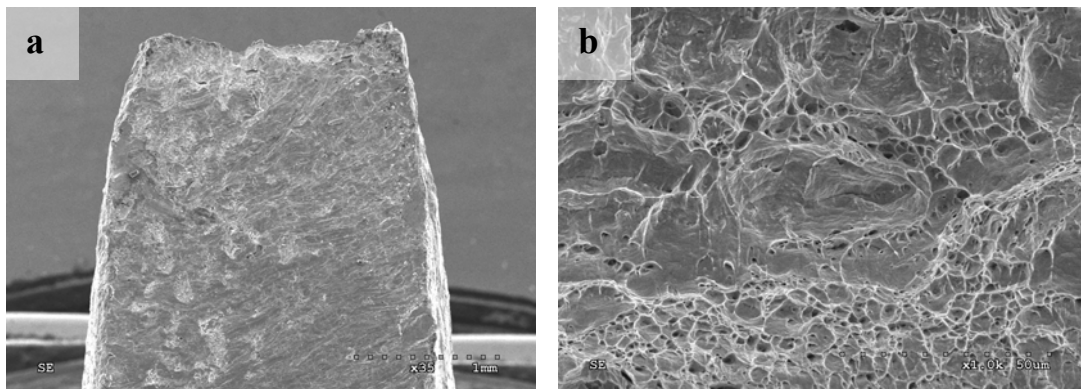


Fig. 3. Lateral surface without cracks of the parent steel – composite I (a) and the ductile fracture surface – composite II of samples tensile tested in air, without hydrogen charging

The fracture surface of samples tested under hydrogen charging of the all composites is brittle and is characterized practically without reduction of area at fraction but by a formation of surface cracks (Fig. 4 *a, b*, and Fig. 5 *a*). An exfoliation along bonding line between flyer and parent metal was not observed under low magnification.

30 thermal cycles did not affect practically the tensile strength of the hydrogenated composite III (Fig. 2 *c*). One can conclude that the hydrogenated composites are less ductile comparatively with the corresponded metal in initial state. The brittle fracture,

exfoliation of the flyer and a presence of surface cracks indicate that the nonlinear part on the curves “ $\sigma - \Delta$ ” is affected by initiation and subcritical crack growth (Fig. 5).

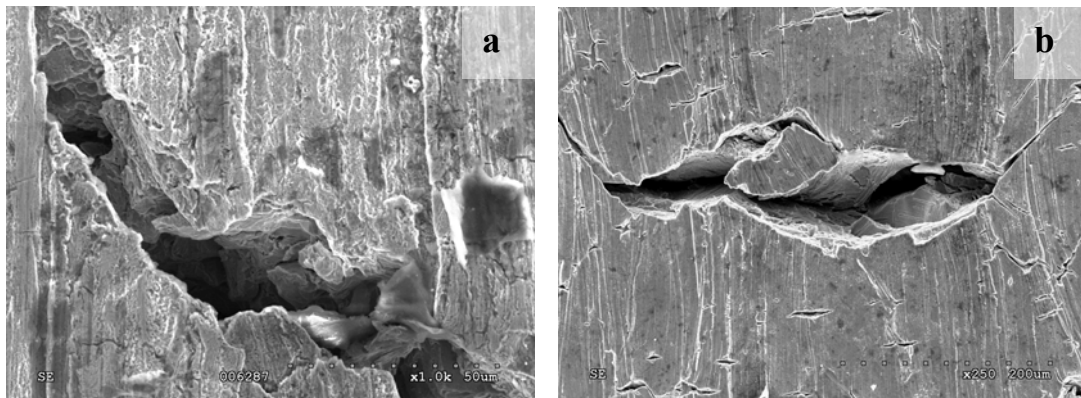


Fig. 4. Hydrogen induced cracks on the lateral surface, close to the fracture surface of the flyer metal of the composite I (a) and composite III (b) hydrogen charged during tensile test

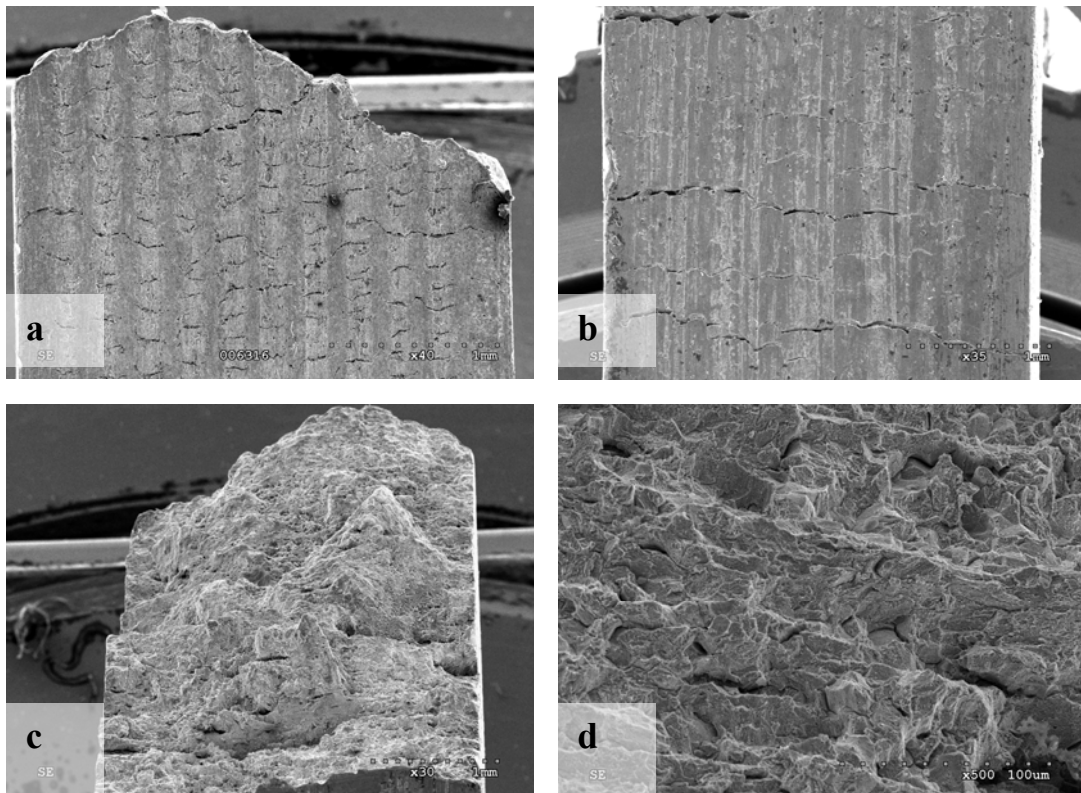


Fig. 5. Lateral surface with many brittle cracks, close to the fracture of the charged parent metal (a) and flyer metal (b) of the composite I. Brittle-ductile fracture surface with secondary cracks of the composite I (c) and composite II (d) after 30 thermal cycles

100 thermal cycles affect essentially the mechanical characteristics and fracture mechanism of the clad metals. This treatment causes a decrease of strength, especially yield strength and is a reason of more brittle mechanism. Fracture of stainless steel begins with flyer exfoliations. Oval defects up to 0.4mm and can be observed. Solitary small cracks are formed on the bonding boundary. It may be admitted that an exfoliation along bonding line took place either during thermocycling or at the beginning of loading. At the bonding line fracture propagates in discrete

steps in the form of terraces. These terraces are decorated by secondary cracks directed in metal bulk in parallel with bonding line. It may be the zone of subcritical crack growth. Hydrogenation embrittles metal additionally, which stipulates plural embrittlement on lateral surfaces of composites especially in stainless steels. There are extensively opened big cracks (0.4÷1.1mm) on the fracture surface of composite I which are expanded from bonding line to both steels of composite. Cracks (nearly 0.5mm) observed on the fracture surface of composite II are more sharp than those ones in composite I. These cracks are formed in stainless steel more preferably. It is possible that cracks were initiated approximately at the same stress level for hydrogenated and unhydrogenated metal as well. However the less deformation to fracture indicates that critical crack length is reached faster when it is caused by hydrogen embrittlement of metal.

CONCLUSIONS

1. The moderate hydrogenation during slow strain rate tension embrittles essentially the composites of low-alloyed steel with stainless steel cladding, however fracture is not accompanied by an exfoliation of the flyer.
2. Thermal cycling of the studied composites in gaseous hydrogen causes brittle fracture at slow strain rate tension in air and also exfoliation of the flyer.
3. Hydrogenation of composites after thermal cycling in gaseous hydrogen embrittles additionally the metals, especially the stainless steels flyers.

ACKNOWLEDGMENTS

This work was supported by the Polish Ministry of Science and High School Education as project 3T08C01228.

REFERENCES

1. Panasyuk V.V., Andreykiv O.Y., Gembara O.V., *Int. J. Hydrogen Energy*. 25/1 (2000), pp. 67-74.
2. Kurzydłowski K.J., Nykyforchyn H., *Problemy Eksploatacji* 51/4 (2003). ss. 7- 18.
3. Nykyforchyn H.M., Student O.Z., Loniuk B.P., *Proc. Polish-Japanese Symp. "Environmental effects on high technology materials"*, Zakopane, 1997. - Warsaw: Inst. Phys. Chem. Polish Academy of Sciences, 1997. pp. 161-166.