Hydrogen Induced Cracking in Duplex 00H18N5M3S Stainless Steel

Krystyna Lublinska[1 a], Andrzej Szummer[1, b], Krzysztof Jan Kurzydlowski[1, c]

[1] Faculty of Materials Science and Engineering Warsaw University of Technology,

Poland 02-507 Warsaw, Woloska 141

aklublin@meil.pw.edu.pl, b aszumm@meil'pw.edu.pl, c kjk@inmat.pw.edu.pl

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Abstract. The interest in the application of duplex stainless steels driven by their advantageous features like comparatively higher strength and superior resistance to stress corrosion cracking to that of austenitic stainless steels. However, under severe conditions, like sulphide/chloride environments or cathodic hydrogen charging, the duplex steels undergo hydrogen embrittlement.

The work presents results of investigations of the mechanism of cathodic hydrogen induced cracking of duplex 00H18N5M3S stainless steel. The techniques used in this investigations included LM (light microscopy), SEM (scanning electron microscopy) and X-ray diffraction.

It was found that hydrogen ingress causes generation of the microcracks and self-induced macrocracks in the ferrite and austenite grains. On the other hand, the X-ray diffraction studies show profound differences in the hydrogen induced expansion of lattice parameters between the austenite and ferrite phases. These differences are the source of high stresses that may play a crucial role in the mechanism of brittle cracking of duplex stainless steels.

Introduction

It is generally known that duplex stainless steels, containing austenite and ferrite, are more resistant to stress corrosion cracking (SCC) than austenitic stainless steels in chloride containing solutions. For this reason, the steels, consisting of at least 50% ferrite, are attractive materials for oil and gas applications particularly off-shore infrastructure exposed to sea water [1,2]. The resistance to SCC in Cl^- containing solutions can be improved by increasing the volume of ferrite phase in a duplex stainless steel [3].

Despite the good resistance to SCC, cracking of these steels induced by hydrogen should be considered. Hydrogen atoms can be generated by corrosion, galvanic interaction between dissimilar metals and by cathodic charging in aqueous solutions. In the applications where cathodic protection is applied or where sour gas or oil is involved with significant amount of hydrogen sulphide, the high fugacity hydrogen increases the likelihood of degradation manifested by a considerable loss in ductility [4,5,6,7].

In this study, the cracking of duplex stainless steel under cathodic applied potential condition in 0.5M H_2SO_4 aqueous solution containing a hydrogen recombination poison, was explored. X-ray diffraction was used for measurements of the hydrogen induced phase transitions and lattice parameters changes of the austenite and ferrite phases. The influence of the solution heat treatment temperature on microstructure, the content and chemical composition of austenite and ferrite and on the hydrogen induced cracking was investigated.

Experimental

The material used in this work was ferritic-austenitic 18Cr-5Ni-3Mo duplex stainless steel. The chemical composition of this steel is given in Table 1.

Table 1. The chemical composition of 18Cr-5Ni-3Mo duplex stainless steel

Element	C	Cr	Ni	Mn	Mo	Cu	S	Si
Wright %	0.042	17.90	4.90	0.28	2.65	0.04	0.019	1.72

Mechanical properties of the studied steel, which was annealed for 10 minutes at 1050ºC in argon atmosphere and subsequently quenched in water, are given in Table 2. These properties were determined in tensile tests conducted in air using INSTRON testing machine.

Table 2. Mechanical properties of 18Cr-5Ni-3Mo duplex stainless steel

$R_{0.2}$ [MPa]	R_m [MPa]	A [%]
402.6	808	28.4

Hydrogen was cathodically introduced into samples by applying a constant current density 0.1 A/cm^2 for 18 hours, at ambient temperature, in 0.5M H_2SO_4 aqueous solution containing 1 mg As_2O_3 per dm^3 as a hydrogen recombination poison (promoter of the entry of the hydrogen atoms into metals). Platinum anode was used.

The X-ray diffraction studies were conducted on the uncharged and H-charged samples using Co Kα radiation. Tests were also conducted on the hydrogen charged samples and aged for 24 hours at room temperature.

In order to determine the influence of the solution heat treatment temperature on the microstructure and chemical composition of the α and γ phases of the studied steel, the samples were annealed for 10 minutes at 1050º, 1250º, 1300º, 1350ºC and quenched in water.

The microstructure of the samples was studied out with the use of light (LM) and scanning electron microscopy (SEM). Samples for observations were grounded using abrasive papers and mechanically polished with the of diamond pastes. One set of samples was electropolished in solution: H_3PO_4 65% + H_2SO_4 12.5% + H_2O 22.5% at 85ºC. (The current density was 200A/cm^2).

The microstructure of the samples was revealed by etching chemical with Murakami solution [8] or electrolytic in 10% oxalic acid at 10-50 mA/cm^2, either before and after hydrogen charging.

Chemical composition of the α-phase and the γ-phase was determined by an electron probe X-ray microanalyser.

Microhardness measurements were carried out with Vickers indenter (Hanemann type) applying a load of 0.196 N.

Results and discussion

Effect of heat treatment on the microstructure and on the chemical composition of the α-phase and the γ-phase

Metallographic investigations have shown that the studied steel after solution heat treatment from 1050˚C has a typical austenitic-ferritic duplex microstructure with relatively fine grains and with nearly equal volume fractions of both phases (Fig. 1 a). An increase of the treatment temperature leads to a decrease in the γ-phase volume fraction and to the grain growth of ferrite. In the samples solution heat treated from1300˚C (Fig. 1 c) and from 1350˚C (Fig. 1 d), the γ-phase was present only in a small quantity, mainly at the boundaries of large ferrite grains (Fig. 1 d).

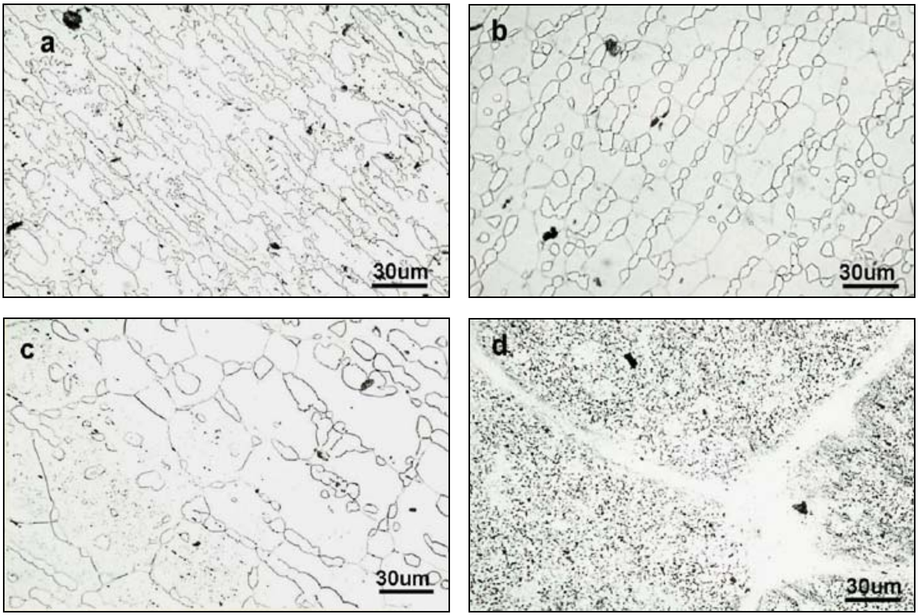

Fig. 1. Microstructure of 18Cr-5Ni-3Mo duplex stainless steel after solution heat treatment from the temperature: 1050ºC – (a), 1150ºC – (b), 1300ºC – (c) and 1350ºC – (d). The specimens etched electrolytically in 10% oxalic acid

Chemical compositions of the α and the γ-phase in samples after solution heat treatment from various temperatures are given in Table 3.

Table 3. The chemical compositions of α-phase and γ-phase in samples after the solution heat treatment

Element Weight [%]	Temperature [^{o}C]					
	1050		1250		1300	
	α-phase	γ-phase	α-phase	γ-phase	α-phase	γ-phase
Si	1.47	1.30	1.57	1.19	1.37	1.38
Cr	18.54	16.10	18.08	17.20	17.51	17.42
Ni	3.69	5.50	4.28	5.72	4.44	4.42
Mo	3.47	2.17	2.69	2.61	2.61	2.61
Fe	72.82	74.93	73.40	73.29	74.07	74.18

It follows from Table 3 that in the case of α-phase the increase of the solution heat treatment temperature lowers the Cr - and increases the Ni content in ferrite grains. On the other hand, in the case of the γ-phase increase in the solution heat treatment temperature increases the Cr - and lowers the Ni content. In the samples solution heat treated from 1300˚C the content of the main alloying elements i.e. Cr, Ni and Mo becomes nearly the same in both (α and γ) phases.

Effect of hydrogen on the structure of 18Cr-5Ni-3Mo duplex stainless steel

X-ray diffraction examinations have shown that cathodic H-charging into 18Cr-5Ni-3Mo duplex stainless steel, like in austenitic grades stainless steels [9-13], induces shifts of diffraction peaks, line broadening and the appearance of new reflections corresponding the formation of hydride phases. Typical results are shown in Fig.2 (B).

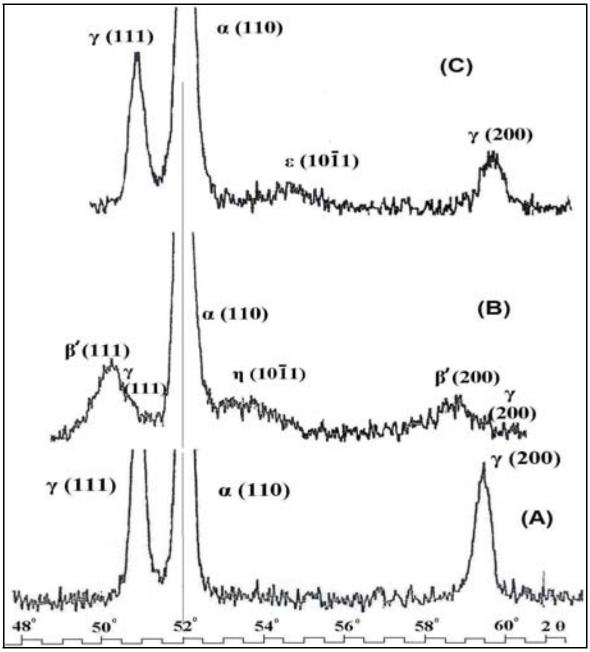

Fig.2. X-ray diffraction pattern of duplex 18Cr-5Ni-3Mo stainless steel. (A) – solution annealed from 1050ºC in uncharged condition (initial state), (B) – cathodic hydrogen charged for 18 hours, (C) – aged at room temperature for 24 hours after cathodic charging

The peaks denoted by β’ [13] which are shifted with respect to γ peaks to lower 2θ angles, originate from f.c.c. hydride phase. This f.c.c. β’ hydride has the same Bravais lattice as austenite but lattice parameter larger in this case by about 1.2 pct [9,13]. The γ phase peaks exhibit also some shifting to smaller 2θ values, consistent with a presence of hydrogen in solid solution. However, due to overlap with β’ peaks, quantitative determination of this change is difficult. It was reported [13] that the f.c.c. γ phase after cathodic charging shows an increase of d-spacings up to 0.7% because of hydrogen in solid solution. Additional peak observed in Fig.2 (B) after hydrogen charging could be indexed as belonging to η hydride phase [13]. This h.c.p. η hydride has the same Bravais lattice as ε martensite (formed a thermally or by plastic deformation of austenite) with the lattice parameter larger up to 5%. This η phase in previous reports was denoted by ε’ [9], by ε* [10], or by Hε [11].

The β’ and η hydrides are unstable at room temperature and under normal pressure decomposing with hydrogen release from the steel. As follows from Fig.2 (C), after 24 hours of aging the diffraction lines from the hydride phases are not present. However, the disappearance of η hydrides is accompanied by formation of h.c.p. ε - martensite – Fig.2 (C). Simultaneously, the γ peaks increase in intensity and shift to higher 2θ values, indicating a decrease of lattice parameter. These results are in agreement with phase transitions in hydrogen charged austenitic stainless steels reported previously in[9-13].

Hydrogen ingress into the α phase also causes shifting the α (110) X-ray diffraction line (Fig.2) to smaller θ values, consistent with the presence of hydrogen in solid solution and an increase of the b.c.c. lattice parameter. This increase was estimated to be up to 0.14% [14]. Aging after cathodic charging at room temperature, releases the hydrogen which diffuses out of the specimen. This results in shifting of the α (110) diffraction peak back to the original 2θ position.

Immediately after charging, the specimen surface appeared distorted when viewed at light magnifications. As outgassing progressed, formation of cracks was observed. Development of these cracks is associated either with considerable variation of lattice parameter, (expansion during charging and contraction during aging), as well as with hydrides formation. The metallic hydrides are typically brittle, and thus their formation can lead to substantial reduction in ductility [15].

Effect of hydrogen on microhardness of the α and γ phases

The results of measurement of microhardness of the α and the γ phases in H-charged samples solution heat treated from 1050ºC are given in Table 4

Table 4. Effect of hydrogen on microhardness of the α-phase and the γ-phase in steel solution heat treated from 1050°C

State of the sample	HV0.02	
	α-phase	γ-phase
Uncharged	419.8	479.0
Hydrogen charged	411.0	659.4
Aged for 24h after hydrogen charging	419.8	525.6

The results in Table 4 are in agreement with previous observations [16] and indicate that H-charging causes distinct increase of microhardness of low nickel content austenite. However, this increase is transient. After 24 hours of aging at room temperature, i.e. after desorption of the hydrogen, microhardness of austenite grains lowers to the similar level as before H-charging.

The characteristic increase of microhardness of low nickel austenite in duplex stainless steel is caused, similarly like in austenitic stainless steels, by the formation of hydride phases [11]. X-ray diffraction confirmed the presence of these phases (β' and η) directly after H-charging (Fig.1). Microhardness of the α-phase grains is lower than that of the γ-phase grains and does not undergo essential changes under H-charging.

Effect of hydrogen on microstructure of 18Cr-5Ni-3Mo duplex steel

Microstructural examinations (light and scanning electron microscopy) showed that hydrogen charging induces numerous microcracks in the low Ni content austenite grains in the duplex 18Cr-5Ni-3Mo steel (Fig.3 and Fig.4). Similar cracks have been observed in the of austenitic grades stainless steels [9, 11, 17]. They form mainly during aging after H-charging, that is during hydrogen desorption due to of variation lattice parameter increases during charging and contracts during aging as outgassing progresses [9, 11-13, 17]. On the other hand in ferrite phase cathodic H-charging brings about different changes in the microstructure. Particularly the surface of ferrite grains formation of H-induced, "grain oriented", needle-shaped microtwins takes place (Figs.3, 4b, 5a). Similar microtwins were observed in ferritic grades stainless steels [14, 18-20]. Inside these microtwins, microcracks are frequently present which run across or along the axis of the needle-shaped microtwins (Fig. 4b). It was also found that hydrogen charging into the duplex stainless steel, especially into samples with the increased volume fraction of ferrite (as a result of solution heat treatment from 1300ºC and 1350ºC) causes formation of "self-induced long cracks" –without action of the applied stresses. These macrocracks run across the ferrite and the austenite grains (Fig.5 and Fig. 6).

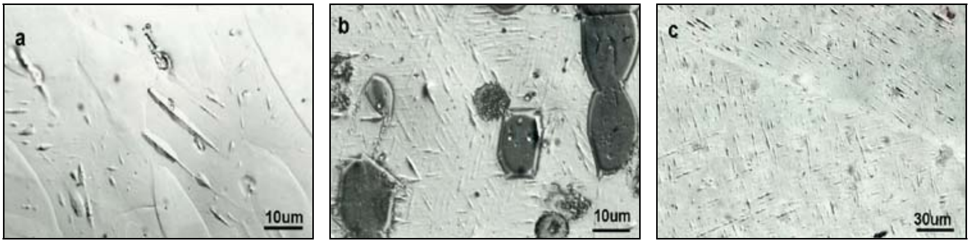

Fig. 3. Microstructure of 18Cr-5Ni-3Mo duplex steel after solution heat treatment from temperature: 1050ºC – (a), 1250ºC – (b), 1350ºC – (c). The specimens after hydrogen charged. (b) – Sample etched chemically with Murakami solution [8]

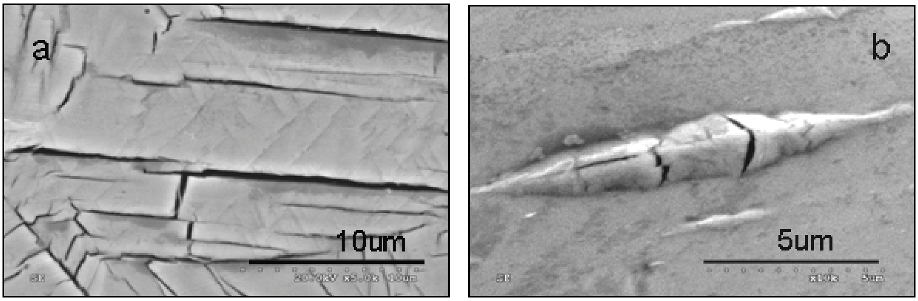

Fig. 4. H-induced microcracks on the surface of austenite grains (a) and the microtwins in the form of needles with microcracks on the surface of ferrite grain

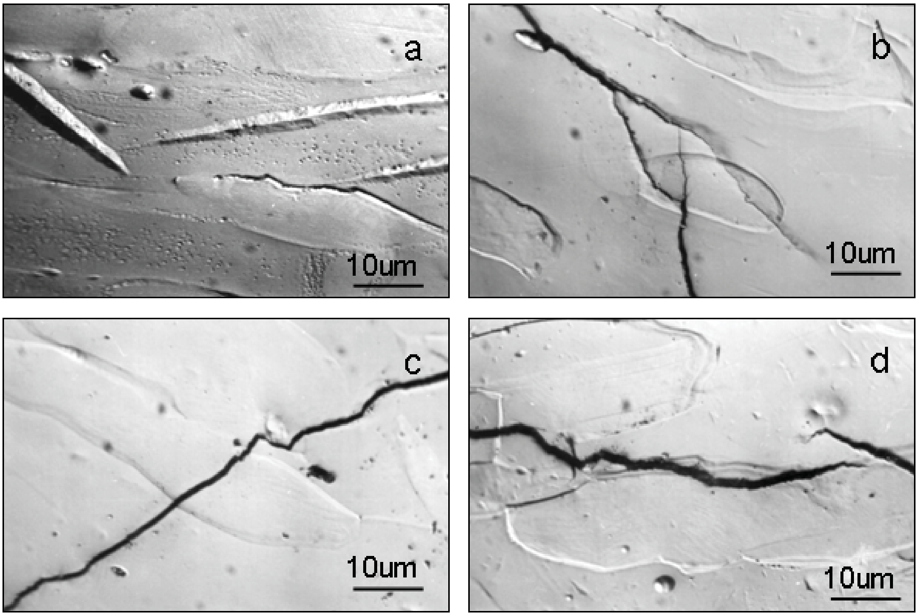

Fig. 5. Microstructure of duplex steel 18Cr-5Ni-3Mo after hydrogen charging. Hydrogen induced needle like microtwins in ferrite grain (a) and cracks (b, c, d)

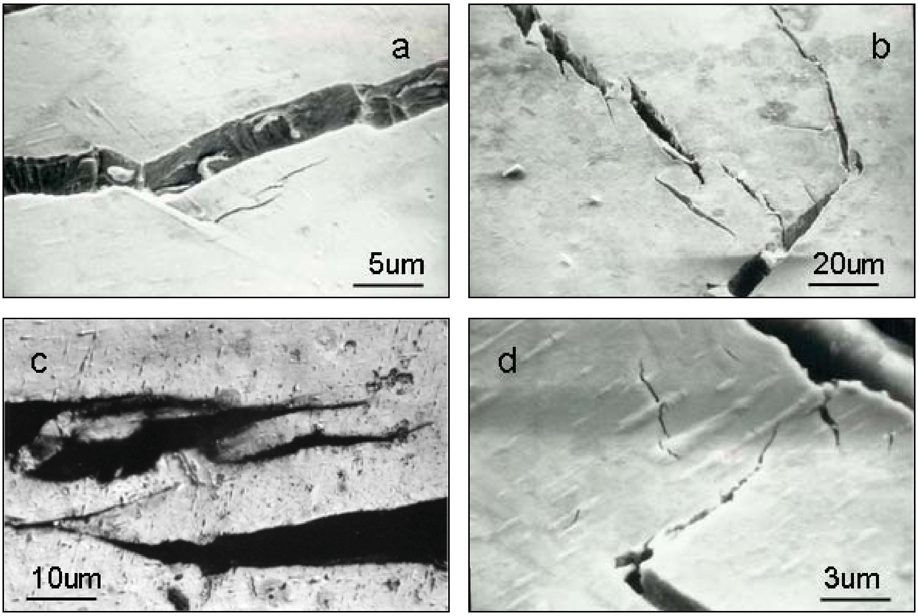

Fig. 6. The self-induced macrocracks on the surface of H-charged 18%Cr-5%Ni-3%Mo duplex stainless steel. Samples after heat treatment at 1350°C

Formation of microcracks in microtwins and macrocracks in ferrite grains, as a result of H-charging, can be explained by the lattice parameter changes because of hydrogen ingress in solid solution during charging and hydrogen egress during aging at room temperature. The hydrogen absorption leads to the lattice expansion and in turn to a volume increase, which generates compression stresses and formation of microtwins. On the other hand, during hydrogen desorption, the decrease of volume takes place, which in turn leads to generation of tensile stresses and formation of cracks in the hydrogen embritteled material. Additional source of high stresses is the large difference in the hydrogen induced lattice parameters expansions between the austenite and ferrite phases. This difference may play a significant role in the mechanism of the brittle macrocracks formation in duplex steel.

Conclusions

Cathodic hydrogen charging into duplex stainless steel 00H18N5M3S brings about generation both the microcracks and macrocracks in the ferrite and austenite grains.

Cracking in austenite grains results mainly from hydrides formation with the associated lattice parameter expansion during H-ingress contraction during aging at room temperature and decomposition of unstable hydrides. These variations are the source of high stresses promoting cracking at microstructures level.

In the ferrite grains H-charging causes formation of microtwins with microcracks inside. These microtwins are “grain oriented” and show a pronounced surface relief, indicating a transition connected with a volume change, probably because of higher concentration of hydrogen inside than in the surrounding matrix. During the aging at room temperature and desorption of hydrogen, the protruding microtwins shrink and microcracks formation takes place. In duplex steel with an increased volume fraction of ferrite phase, as a result of solution heat treatment from higher temperature, H-charging causes large macrocracks formation. A large difference in the hydrogen induced lattice parameters expansions between the austenite and ferrite phases may play a crucial role in formation of these macrocracks.

Acknowledgment

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