This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

He, Jinshan; Guo, Xiaofei; Lian, Junhe; Münstermann, Sebastian; Bleck, Wolfgang
Delayed cracking behavior of a meta-stable austenitic stainless steel under bending condition

Published in:
MATERIALS SCIENCE AND ENGINEERING A: STRUCTURAL MATERIALS PROPERTIES
MICROSTRUCTURE AND PROCESSING

DOI:
[10.1016/j.msea.2019.138470](https://doi.org/10.1016/j.msea.2019.138470)

Published: 19/12/2019

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:
He, J., Guo, X., Lian, J., Münstermann, S., & Bleck, W. (2019). Delayed cracking behavior of a meta-stable austenitic stainless steel under bending condition. *MATERIALS SCIENCE AND ENGINEERING A: STRUCTURAL MATERIALS PROPERTIES MICROSTRUCTURE AND PROCESSING*, 768, [138470].
<https://doi.org/10.1016/j.msea.2019.138470>

Journal Pre-proof

Delayed cracking behavior of a meta-stable austenitic stainless steel under bending condition

Jinshan He, Xiaofei Guo, Junhe Lian, Sebastian Münstermann, Wolfgang Bleck

PII: S0921-5093(19)31256-0

DOI: <https://doi.org/10.1016/j.msea.2019.138470>

Reference: MSA 138470

To appear in: *Materials Science & Engineering A*

Received Date: 3 July 2019

Revised Date: 26 September 2019

Accepted Date: 27 September 2019

Please cite this article as: J. He, X. Guo, J. Lian, S. Münstermann, W. Bleck, Delayed cracking behavior of a meta-stable austenitic stainless steel under bending condition, *Materials Science & Engineering A* (2019), doi: <https://doi.org/10.1016/j.msea.2019.138470>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier B.V.

Delayed cracking behavior of a meta-stable austenitic stainless steel under bending condition

Jinshan He^{1,2}, Xiaofei Guo^{2*}, Junhe Lian^{3,4}, Sebastian Münstermann², Wolfgang Bleck²

1) Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, P. R. China

2) Steel Institute, RWTH Aachen University, Aachen 52072, Germany

3) Department of Mechanical Engineering, Aalto University, Puumiehenkuja 3, 02150 Espoo, Finland

4) Impact and Crashworthiness Lab, Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

Abstract

The delayed cracking behavior of a meta-stable austenitic stainless steel AISI 301 under bending condition has been investigated at different temperatures, hydrogen contents and external holding forces. The results reveal that the investigated material with an initial hydrogen content of 1 ppm has good bendability at the temperature range between -20 °C and room temperature, which is not susceptible to delayed cracking in atmospheric condition. When the material is pre-charged with 50 ppm hydrogen, the material still shows good bendability. However, it is susceptible to delayed cracking under an external holding force during interrupted bending test. By the measurement of martensitic transformation, the simulation of the stress/strain distributions in the bending specimens and the characterization of fracture surfaces, the effects of hydrogen, stress state and external holding force on delayed cracking behavior have been assessed.

* Corresponding author. Tel.: +49-241-8095809; Fax: +49-241-8092253;

E-mail address: xiaofei.guo@iehk.rwth-aachen.de

1 Introduction

Owing to the combination of excellent corrosion resistance, work hardenability and formability, AISI 301 austenitic stainless steel attracts much attention for industrial applications. The ultra-high strength of this material attributes to the transformation induced plasticity (TRIP) effect, in which the dynamic austenite-to-martensite transformation takes place during the metal forming process [1-3]. This phase transformation accomplishes through the coordinated shape and volume changes by short-distance atomic movement under the driving force of strain and stress. The TRIP effect also extends the uniform elongation by postponing the occurrence of necking [4,5]. Consequently, the formability, particularly the deep drawability of austenitic stainless steels has been effectively improved [3-5]. However, the deformation induced martensitic transformation may raise the material susceptibility to delayed cracking (DC) after forming [6-10], since it induces residual stress and affects both the solubility and diffusivity of hydrogen. Cracks occur unpredictably in successfully formed components after hours, days or even weeks, raising substantial reliability and safety risks.

Many studies have been carried out to investigate the influence of austenite stability on delayed cracking behavior [6-12]. The strain induced martensitic transformation leads to high residual stress in meta-stable austenitic stainless steels, which may trigger crack initiation, especially in hydrogen-rich environment [6-9]. In addition, the role of internal hydrogen in delayed cracking of different metastable austenitic stainless steels has been intensively investigated [10, 11, 13-17]. Hydrogen is a type of interstitial element with high solubility in face-centered cubic (fcc) lattice structure. It has been reported that hydrogen effectively enhances dislocation emission and raises dislocation mobility, which is interpreted as the hydrogen enhanced localized plasticity (HELP) mechanism [10, 11]. Nibur et.al observed slip planarity in austenitic stainless steel with the presence of hydrogen [11]. They clarified that hydrogen stabilized the edge component of dislocations and inhibited the cross slip [11]. When the strain induced α' martensite forms at the intersections of ϵ martensite or dislocation pile-ups [12], hydrogen accumulation will be further facilitated as a result of the local high hydrostatic stress [13]. Hua et al. observed the enrichment of hydrogen at twin boundaries in association with the formed α' martensite in an austenitic stainless steel AISI 304 by scanning kelvin probe force microscopy [14]. It is also reported that the formed α' martensite plays an important role in accelerating hydrogen diffusion [15-17], which acts as “highway” for hydrogen transportation to austenite matrix. The hydrogen diffusivity in martensite is reported around 5-6 orders higher than that in austenite [17]. Zhang et. al. applied hydrogen release measurement during tensile test and observed that hydrogen releasing was closely related to the crack initiation between the martensite and austenite-rich zones, which further propagated in α' martensite phase [16]. The macroscopic brittle feature also supports the hydrogen enhanced decohesion (HEDE) theory [18, 19], which states that hydrogen reduces the atomic bonding energy and lead to cleavage fracture. The strain induced α' martensitic formation ahead of notch tip is assumed to be the main reason for the high HE susceptibility in metastable austenitic stainless steels [20]. It was found that the subcritical cracking induced by hydrogen was typically time-dependent and some researchers described the crack propagation with stress-intensity in structural metal components under static loads [21-23]. DC behavior has been widely studied by deep drawing tests, however, applications at such high stress and strain levels are not often found in practice. Furthermore, the high sensitivity to DC in deep drawing condition makes the quantitative investigation of the mentioned influencing factors difficult. Even though slow strain rate tests under uniaxial tension load

condition are frequently used as quantitative investigation methods; these tests cannot fully represent the service condition of steels. Moreover, the stress state was identified significantly affecting crack initiation mechanisms, i.e. the fracture strain varied significantly at different stress states [24, 25].

Bending is frequently used during manufacturing components by cold forming, which introduces multi-axial stress conditions. Therefore, the present study focuses on the delayed cracking behavior of meta-stable austenitic stainless steel AISI 301 under bending condition. The influences of deformation temperature, hydrogen content and external holding force on delayed cracking behavior are considered in the current investigation. Finite element simulation with Abaqus software is performed to describe the strain and stress distributions in the bending specimens. The martensite distributions in the bending specimens are further characterized by Ferritscope and electron backscattering diffraction (EBSD), which are correlated with the crack propagation features on the bending head without and with diffusive hydrogen.

2. Material and experimental procedures

Industrially processed austenitic stainless steel AISI 301 was investigated in the study. The cold rolled sheet with a thickness of 1 mm was supplied in annealed condition with 2B surface finish according to EN 10088-2. The chemical composition is listed in Tab. 1. The material has an austenitic microstructure with 1% dispersed α' martensite in volume fraction, which was quantified by Ferritscope measurement. The average grain size of the austenite phase is 24 μm .

Tab. 1. Chemical composition of the investigated AISI 301 steel.

	C	Si	Mn	Cr	Mo	Ni	Cu	Nb	N	H (ppm)
wt.%	0.097	1.09	1.22	16.73	0.67	6.83	0.27	0.005	0.019	1.08

The mechanical properties of steel AISI 301 were measured by quasi-static tensile tests at a strain rate of 0.01 s^{-1} with a universal tensile machine Zwick Z100/TL3S. Specimens with the gauge length of 80 mm were manufactured according to EN 10002. Three-point bending tests were performed on a universal testing machine Zwick 1445 with a punch radius of 1 mm and a punch speed of 1 mm/s. As shown in Fig. 1(a), the specimen has a geometry of 80 mm in length and 13 mm in width. The deformed specimen has a bending head with an inner radius of 1 mm. The bending tests were performed at 23°C (room temperature), 0°C and -20°C, which were realized by liquid nitrogen cooling and combined thermocouple measurement.

The average martensitic fraction throughout the sheet thickness was measured with a Ferritscope (FISCHERSCOPE MMS) with the measuring probe EGAB 1.3FE. As shown in Fig. 1(b), the martensite fraction was measured from the center of the bending head till a distance of 15 mm away. Since Ferritscope is designed to measure ferrite fraction based on magnetic inductive process, the measured magnetic phase fraction is converted to a martensitic fraction by multiplying a correction factor of 1.7, as calibrated in previous studies [7, 26].

To investigate hydrogen influence on delayed cracking behavior, the specimens were galvanostatically charged for 25 hours in 0.5 M H_2SO_4 solution with 0.25 g/l As_2O_3 at a

constant current density of 20 mA/cm^2 at 50°C . A platinum plate with the geometry of $80 \times 50 \text{ mm}$ was used as an anode, while the specimen worked as a cathode. After hydrogen charging, the specimens were dwelled at room temperature for 24 hours before performing the bending tests. The dwelling process desorbed supersaturated hydrogen at the surface and enabled more homogeneous distribution of hydrogen in the sub-surface. The hydrogen concentration in the cathodic charged specimens was measured after dwelling at room temperature for 24 hours by LECO RH-402 hydrogen determinator based on hot extraction method. The molecule hydrogen was carried by flowing nitrogen gas and measured by thermal conductivity, which offers an accuracy of above $\pm 0.1 \text{ ppm}$.

Fig. 1. (a) Original and deformed specimen and (b) The positions for the measurement of martensitic fraction, starting from the center point of the bending head.

To characterize the strain and stress states of the critical points on the bending specimens, corresponding numerical simulations were performed using the finite element (FE) code Abaqus/Explicit. A full model was set up for the bending tests. The model was meshed using three-dimensional (3D) eight-node continuum elements with reduced integration (C3D8R). A similar mesh strategy was adopted as described in a previous work [27]: the mesh size of the critical part is 0.2 mm , while that of the rest can be relatively larger. The punch and support rollers were modelled as rigid solids and the Coulomb friction value was assumed to be 0.1 at the interface by considering the contact situation between rollers and samples. Two bottom rollers were set fixed in all degree freedoms. The bottom roller was lifted up to bend the specimens under the applied experimental condition. The stress or strain distributions taken from the simulation results were according to the corresponding roller displacements in the experiments. Without considering the stress state effect on the flow curve associated with phase transformation, the von Mises plasticity is applied in the simulation to show the stress and strain distribution. Therefore, we must admit that the simulated results based on the phenomenological model lack certain accuracy. However, the simulations give information about the strain and stress levels and distribution profiles at different bending stages, which is useful for the associate discussions.

The fracture surfaces on the delayed fractured bending specimens were characterized by Zeiss Sigma field-emission scanning electron microscope (SEM) at the operation voltage of 15 kV . The microstructure at the bending head was further analyzed using EBSD with a step size of 100 nm and then the data was processed with the software Atec.

3. Results

3.1 Tensile properties at different temperatures

The stress-strain curves at different temperatures were obtained by tensile tests. Fig. 2 (a) shows the engineering stress - strain curves of the steel AISI 301 at different temperatures. It is found that the tensile strengths are 1158, 1091 and 923 MPa respectively. The fracture strains have reached 0.38, 0.49 and 0.49 respectively at $-20\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$ and $23\text{ }^{\circ}\text{C}$. Fig. 2(b) presents all flow curves at different tensile temperatures. Obviously, the temperature has a strong influence on the mechanical response of the steel. The strain hardening rate increases with the decrease of temperature. The work hardening is related to the generation of dislocation structures. On the other hand, the steel shows a strong TRIP effect. Since transformed martensite has a higher initial flow stress than austenite, substantial dislocations are inherited by the transformed martensite and the austenite-martensite interfaces [12, 28]. The flow curves were subsequently imported into Abaqus software for simulating the strain and stress evolution during the bending process. Consequently, the effects of stress state on martensite formation were studied by this approach.

Fig. 2. (a) Engineering stress-engineering strain and (b) True stress-true strain curves of AISI 301 at the temperature range from $-20\text{ }^{\circ}\text{C}$ to $23\text{ }^{\circ}\text{C}$.

3.2 Bending tests at different temperatures

The bending tests were performed at temperatures of $-20\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$ and $23\text{ }^{\circ}\text{C}$ till a complete U-bending stage, as shown in Fig. 1 (a). After these tests, no cracks were observed on the surface of bending heads of these specimens. The force-displacement curves in Fig. 3 (a) indicate that high force is implemented to have same deformation at low temperature. The average martensite contents on the bending specimens at the center of bending head measured by Ferritscope are shown in Fig. 3 (b). The volume fractions of martensite increase from 39% to 51% at the center point of bending head when the temperature of bending decreases from -20 to $23\text{ }^{\circ}\text{C}$. With the help of the corresponding simulation, the equivalent plastic strain and maximum principal stress contours at different temperatures for the bending specimens could be analyzed, as shown in Fig. 4. Both the maximum principal stress and equivalent plastic strain at the center point of the outer edge after bending were summarized in Tab. 2. It is observed that the strain of the center point of the bending specimens are similar, but the local stress and the fraction of martensite are relatively larger with the decrease of temperature. The investigated material shows very good bendability at the temperature range from $-20\text{ }^{\circ}\text{C}$ to $23\text{ }^{\circ}\text{C}$ without showing any crack induced by deformation.

Fig. 3. (a) Force-displacement curves for bending tests and (b) Distribution of martensite fraction from the center point of bending head till 15 mm away in the bending specimens deformed at -20 °C, 0 °C and 23 °C.

Fig. 4. The contour of equivalent plastic strain (left) and principal stress (right) in the bending specimens at the stage when the U-bending is completed at (a) -20 °C, (b) 0 °C and (c) 23 °C.

Tab. 2: Parameters at the center point of the bending head at different temperatures.

Bending temperature, °C	Equivalent plastic strain (simulation)	Max. principal stress σ_1 , MPa (simulation)	Max. α' , vol.% (measured)	Crack initiation status
-20	0.35	1720	51	no cracks
0	0.34	1628	47	no cracks
23	0.34	1370	39	no cracks

3.3 Fracture evolution in hydrogen pre-charged bending specimens holding for different periods

The hydrogen effect on the bendability was investigated by using samples with electrochemical pre-charged hydrogen. The hydrogen concentrations of the material have reached 50 ± 3 ppm after hydrogen charging for 25 hours with subsequent 24 hours dwelling at room temperature, as measured by hot extraction method. Bending tests on specimens with 50 ppm pre-charged hydrogen were interrupted and held at a bending force of 1.6 kN for different periods. Fig. 5 shows the SEM images at the outer surfaces of these specimens. Under such conditions, the transformed martensitic volume fractions reached 50.8%, 50.6% and 51.6% for 1, 5 and 16 hours respectively, which were measured by Ferritscope. The crack nuclei may exist due to the local stress instabilities caused by surface embrittlement. After 1 hour holding at 1.6 kN, no micro-cracks can be seen. After 5 hours holding at 1.6 kN, micro-cracks propagated along the width direction of specimens. The number and size of the micro-cracks increased with the increased holding time. When they reached the critical size, the steel lost its stiffness and the holding force dropped conspicuously. Subsequently, the micro-cracks linked together and grew into larger cracks in parallel to the punch head, as seen in Fig. 5(c).

Fig. 5. The outer surfaces of the bending specimens with 50 ppm hydrogen holding at the bending force of 1.6 kN for (a)1 h, (b)5 h and (c)16 h.

3.4 Fracture evolution in hydrogen pre-charged bending specimens holding at different forces

In order to investigate the effect of holding force on delayed cracking behavior, the bending tests were interrupted at bending forces between 0.5 kN and 1.6 kN and held continuously for 24 hours to trace the crack initiation status. Fig. 6 (a) reveals the evolution of holding force when the specimens with 1 and 50 ppm hydrogen were interrupted and held at the holding force of 1.6 kN for 24 hours. It can be seen that the holding force was almost constant for the

specimen with 1 ppm hydrogen. But for the specimen pre-charged with 50 ppm hydrogen, the force dropped drastically after holding for about 2.7 h, which can be deemed as the occurrence of delayed fracture. The time till the force reduction is regarded as the incubation time, which is corresponding to time for the growth of crack nuclei to macroscopic cracks that cause material failure. The incubation time accounts for 2.7 hours for the specimen with 50 ppm hydrogen held at the bending force of 1.6 kN. Fig. 6 (b) shows the correlation between the applied holding force (F_H) and the incubation time till the initiation of DC (t_F), which follows a negative exponential correlation as fitted by the dashed line and described in Equation (1).

$$t_F = 46.9 e^{-2.0 \times F_H} \quad \text{Equation (1)}$$

As seen in Fig. 6 (b), the experimental data are close to the fitting curve, validating the effectiveness of equation (1). Tab. 3. lists the simulated strain, stress and measured martensite volume fraction at the central point of the bending heads for specimens at different holding forces. Based on the numerical simulations, the holding force can also be replaced by the applied equivalent plastic strain ϵ_v , equation (2). It also indicates the negative exponential dependence of incubation time to delayed cracking on the equivalent plastic strain.

$$t_F = 34.8 e^{-7.7 \times \epsilon_v} \quad \text{Equation (2)}$$

Fig. 6. (a) The evolution of holding force within 24 hours holding time and (b) the dependence of incubation time till crack initiation on the applied holding forces in 50 ppm hydrogen pre-charged specimens bended at -20°C .

Tab. 3. The strain, stress and martensite volume fraction at the central point of the bending heads in bending specimens at different holding forces.

H content	Holding force F_H	Holding time	Equiv. plastic strain ϵ_v	Max. principal stress σ_1	Hydrostatic stress σ_h	Max. α'	Crack behaviors
ppm	kN	hour	-	MPa	MPa	vol. %	hour
50	0.5	24	0.097	652	316	39	$t_F=20.1 \pm 0.8$ h
50	0.8	24	0.19	1342	647	48	$t_F=10.2$ h
50	1.6	24	0.35	1720	850	54	$t_F=2.5 \pm 0.2$ h
1	1.6	24	0.35	1720	850	51	No cracks

Fig. 7 reveals morphologies of the outer surfaces of specimens after holding at different forces for 24 hours. As observed in Fig. 7(a), there is no crack for the specimen which contains only 1 ppm hydrogen. But for other specimens shown in Fig. 7(b) and (c), there are large amounts of cracks. The density and the depth of these cracks increased as the holding forces were raised. All the cracks revealed cleavage fracture with rugged surfaces, as seen in Fig. 7(d), which is associated with the transformed martensite.

Fig. 7. SEM images of the outer surfaces at the bending head after holding at different forces for 24 hours: (a) the bending specimen with 1 ppm hydrogen and holding at 1.6 kN; (b) the bending specimen with 50 ppm hydrogen and holding at 0.8 kN; (c) the bending specimen with 50 ppm hydrogen and holding at 1.6 kN; (d) is the magnified image of the marked square region in (c).

3.5 EBSD analysis

To investigate the influence of stress state on martensitic transformation, an inner region and an outer region along the central line of the bending head were examined with EBSD. The specimen was bended at the temperature of $-20\text{ }^{\circ}\text{C}$. According to the simulation in Fig. 4 (c), the most inside node (in the inner region) along the central line sustains to compressive stress of 342 MPa and equivalent strain of 0.32. The most outside node (in the outer region) along the central line sustains to tensile stress of 1720 MPa and equivalent strain of 0.35. Fig. 8 shows the phase distribution maps and rolling direction (RD)-Inverse pole figure maps from the inner region and outer region, which are in the size of $60\times 90\text{ }\mu\text{m}^2$. Three phases were observed in both areas: austenite (fcc), α' martensite (bcc) and ϵ martensite (hcp). The outer region endured much more severe martensitic transformation compared to the inner region, which proves the pronounced effect of stress state on phase transformation as described in [29].

Fig. 8. Phase distribution maps and RD-Inverse pole figure maps at the inner and outer regions along the central line of the bending head.

On the other hand, to investigate the delayed cracking behavior in hydrogen pre-charged bending specimens, the outer region with the size of $50 \times 50 \mu\text{m}^2$ was examined with EBSD, as shown in Fig. 9. It was found that the crack initiated in the martensite since there was almost no retained austenite phase at the outer region. The crack nucleated along the prior austenite grain boundaries, as indicated by the Inverse pole figure map. It further propagated transgranularly through the lath of transformed α' martensite, which was in consistence with the observed zig-zag surfaces of the cracks on the surface of bending head, as shown in Fig. 7(d).

Fig. 9. Phase distribution map and RD-Inverse pole figure map at outer region along the central line of the bending head in 50 ppm hydrogen pre-charged specimen. The white dashed line indicates the crack.

4. Discussion

4.1 Temperature effect on the martensitic transformation

Based on the analysis of martensite fraction on the bending specimens in Fig. 3(b) and Tab. 2, it was found that the austenite to martensite transformation was accelerated at low temperature due to the high chemical driving force that overcomes the transformation energy barrier [12]. The maximum α' martensite content was raised from 39% to 51% in the investigated material by varying the bending temperature from room temperature to $-20\text{ }^{\circ}\text{C}$. It is reported that the ϵ martensite forms along with stacking faults [12], while α' martensite prefers nucleating at intersections of shear bands, which consist of bundles of faults, twins and ϵ martensite [12, 29, 30]. As revealed by the EBSD analysis in Fig. 8, the transformed martensite is mainly the α' martensite. The simulation results in Fig. 4 reveal that the equivalent strain at the center of the bending head approaches 0.35. The tensile stress varies from 1370 -1720 MPa, which is due to the temperature effect on the martensitic transformation. The austenite stability of stainless steel is normally empirically evaluated by the temperature Md_{30} at which 50% martensite is formed at a true strain of 0.3. According to reference [31], the empirical equation to calculate Md_{30} is described in Equation (3):

$$Md_{30} = 551 - 462 \times (\%C + \%N) - 9.2 \times (\%Si) - 8.1 \times (\%Mn) - 13.7 \times (\%Cr) - 29 \times (\%Ni + \%Cu) - 18.5 \times (\%Mo) - 68 \times (\%Nb) - 1.42 \times (G - 8)$$

Equation (3)

where G is grain size number according to ASTM standard. With the chemical composition listed in Tab. 1, the Md_{30} is calculated to be $38.6\text{ }^{\circ}\text{C}$, which indicates extensive α' martensite formation at room temperature.

4.2 Stress state effect on martensitic transformation and delayed cracking behavior

The FEM simulation in Fig. 4 reveals the inhomogeneity of strain and stress distribution along the thickness direction in the region near the bending head. The EBSD results of both inner edge and outer edge at the bending head further indicate the inhomogeneous martensitic transformation throughout the sample thickness, which is directly correlated to the local stress state. After statistical study of the phase distribution in Fig. 8, the area at the inner edge is composed of 42.1% austenite, 55.8% α' martensite and 0.9% ϵ martensite, while the area at the outer edge is composed of 4.1% austenite, 94.5% α' martensite and 0.3% ϵ martensite. Obviously, there is much more austenite transformed to martensite at the outer edge than that at inner edge. This can be attributed to the different stress states at the outer and inner edge. By extracting parameters from simulation, the stress triaxiality and Lode angle at the outer edge are 0.39 and 1 respectively, which are between the uniaxial and plane-strain tensile stress state. In comparison, they are -0.49 and -0.37 respectively at the inner edge, which are in the compressive stress state. As reported in previous literatures [32, 33], more martensite will be developed under tension than that under compression. In this research, the EBSD measurements revealed that the fraction of transformed martensite increased with the raised stress triaxiality and Lode angle parameter.

The EBSD results of 50 ppm pre-charged bending specimen, as shown in Fig. 9, revealed that the crack originated from the martensite at the outer edge. This is because martensite can serve as a fast diffusion path for hydrogen to induce potential crack initiation [16,17,34]. It also indicated the transformed martensite had higher sensitivity to hydrogen embrittlement compared to austenite [20]. As a result, the outer edge revealed high delayed cracking susceptibility at hydrogen pre-charged condition due to the strain induced martensitic transformation and high tensile stress. In comparison, no cracks at the inner edge were observed owing to the compressive stress state.

4.3 Hydrogen effect on martensitic transformation and delayed cracking behavior

In the investigated material, hydrogen does not reveal strong effect on martensitic transformation. The martensite fraction measured by Ferritscope at the center point of the bending head is 51% and 54% for the uncharged and the 50ppm hydrogen pre-charged conditions after bending at -20 °C respectively, as listed in Tab.3. The stress and strain state are almost the same since they were bended at the same forming parameters.

The quite different DC behaviors shown in Fig. 7 (a) and (c) indicated the important role of hydrogen in DC. In other words, even though a large amount of martensite has been induced, DC will not occur in the investigated material without introducing sufficient hydrogen. The rugged fracture morphology near surface region in Fig. 7 (d) indicated the decohesion at the martensitic lath interfaces, which has zigzag trans-granular feature. This fracture feature has been observed also in other meta-stable austenitic stainless steels [14-17, 35,36]. Koyama et al. explained that it may be due to the supersaturated hydrogen causing decohesion along the typical cleavage planes, e.g. $\{100\}_{\alpha}$ plane of α' martensite [15]. The current study also observed that the crack propagated closely along the $\{100\}_{\alpha}$ plane and grain boundaries, as shown in Fig. 9. Therefore, it is possible that hydrogen reduced the cohesive energy of the grain boundary as well as the cleavage planes. The brittle nature of transformed α' martensite with supersaturated hydrogen drove the decohesion of cleavage planes. On the other hand, hydrogen was identified as enhancing local plastic deformations by the observations of promoted martensitic transformation near crack tips [17,20,35,36] in meta-stable austenitic stainless steel. In the investigated steel, the raised amounts of transformed martensite were

also measured in hydrogen charged condition by Ferritscope as well as by EBSD, which may also attribute to the hydrogen enhanced localized plasticity. The transformed martensite coupled with the applied external holding force led to hydrogen enrichment at the crack tips and continuous crack propagation [13,35-37].

4.4 Influences of external holding forces on delayed cracking behavior

The fitting curves of Equation (1) and (2) indicate that delayed cracks propagate earlier at larger holding force. According to the references [21,22], there is a threshold stress intensity for the onset of subcritical cracking, which has a negative correlation with hydrogen concentration. Since hydrogen concentration increases negative exponentially with rising hydrostatic stress, the threshold stress intensity also drops with the hydrogen concentration [19, 23]. As seen in Tab. 3, the hydrostatic stress increases with the external holding force. Therefore, the threshold stress intensity of the specimen with large external holding force is smaller. In addition, since stress intensity of the specimen has a positive correlation with the maximum principal stress, bending specimen with large external holding force will reach threshold stress intensity for the onset of subcritical cracking earlier. Therefore, the incubation time to delayed cracking is shorter for the bending specimens with larger external holding force.

The incubation process of delayed cracking can be described by the following stages. In the first stage, the 50 ppm hydrogen pre-charged bending specimens have been held at a certain holding force, crack nuclei may exist due to the local stress instabilities caused by surface embrittlement. Before reaching the critical stress, the stress intensity of the bending specimen is not large enough for subcritical cracking. Therefore, the micro-cracks do not grow. With a time effect, the pre-charged hydrogen will diffuse to the region with high hydrostatic stress [13]. Hydrogen accumulation plays a strong role in reducing the threshold stress intensity [21-23]. After threshold stress intensity of the specimen declines sufficiently, the micro-cracks grow. During the crack propagation, the stress intensity is increasing since the crack length grows gradually. Then it becomes easier to reach the local stress instability. Finally, the micro-cracks link with each other and grow into macro-cracks. The holding forces dropped when the mechanical instability was fulfilled. When the external holding force is large, the stress intensity of the specimen is large. Shorter time for hydrogen accumulation is need. Therefore, the incubation time declined with the raising external holding force, as described in Fig. 6 (b).

5. Conclusions

The delayed cracking behavior of AISI 301 stainless steel has been investigated with a hybrid approach combining experiment and simulation. The following conclusions can be summarized.

- 1) The temperature, strain level and stress state affect the martensitic transformation. With the increasing strain, stress triaxiality and Lode angle as well as with the decreasing temperature, martensitic transformation is promoted after bending, which introduces more hydrogen quick-diffusion paths and crack initiation sites for delayed cracking.
- 2) Hydrogen content in the steel is critical for the occurrence of delayed cracking. With low hydrogen content of 1 ppm in the specimens, delayed cracking will not happen at the outer surface with as high as 94.5% α' martensite. With 50 ppm pre-charged hydrogen, the delayed cracking occurs in hours, following negative

exponential correlations with the applied holding force and maximum equivalent strain.

- 3) Delayed cracking initiates at the outer surface, since the outer surface is in the tension stress state where martensitic transformation is promoted, and hydrogen diffusion is facilitated.

Acknowledgements

Partial of this research work is financially supported by the Materials Innovation Institute (M2i), the Netherlands and the Philips Company under the project number MC 1.05228. The first author would like to acknowledge the financial support of the China Scholarship Council (CSC).

References

- [1] V.F. Zackay, E.R. Parker, D. Fahr, R. Busch; The enhancement of ductility in high-strength steels, *ASM Transactions Quarterly* 60(2) (1967) 252-259.
- [2] V.F. Bhandarkar, V.F. Zackay, E.R. Parker; Stability and mechanical properties of some metastable austenitic steels, *Metallurgical Transactions* 3 (1972) 2619-2631.
- [3] V. Talyan, R. H. Wagoner, J. K. Lee; Formability of stainless steel, *Metallurgical and Materials Transactions A* 29 (1998) 2161-2172.
- [4] A.A. Lebedev, V.V. Kosarchuk; Influence of phase transformations on the mechanical properties of austenitic stainless steels, *International Journal of Plasticity* 16(7) (2000) 749-767.
- [5] W. Bleck, X.F. Guo, Y. Ma; The TRIP effect and its application in cold formable sheet steels, *Steel Research International* 88(10) (2017) 1700218.
- [6] M.R. Berrahmoune, S. Berveiller, K. Inal, E. Patoor; Delayed cracking in 301LN austenitic steel after deep drawing: Martensitic transformation and residual stress analysis, *Materials Science and Engineering A* 438-440 (2006) 262-266.
- [7] X.F. Guo, J. Post, M. Groen, W. Bleck; Stress oriented delayed cracking induced by dynamic martensitic transformation in meta-stable austenitic stainless steels, *Steel Research International* 82(1) (2011) 6-13.
- [8] S. Papula, J. Talonen, H. Hänninen; Effect of residual stress and strain-Induced α' martensite on delayed cracking of metastable austenitic stainless steels, *Metallurgical and Materials Transactions A* 45(3) (2014) 1238-1246.
- [9] S. Papula, T. Saukkonen, J. Talonen, H. Hänninen; Delayed cracking of metastable austenitic stainless steels after deep drawing, *ISIJ International* 55(10) (2015) 2182-2188.
- [10] C. San Marchi, K. A. Nibur, D. K. Balch, B. P. Somerday, X. Tang, G. H. Schiroky, T. Michler; Hydrogen assisted fracture of austenitic stainless steels, *Proceedings of the 2008 International Hydrogen Conferences, ASM*, (2009) 88-96.
- [11] K.A. Nibur, D.F. Bahr, B.P. Somerday; Hydrogen effects on dislocation activity in austenitic stainless steel, *Acta Materialia*, 54(10) (2006) 2677-2684.
- [12] G.B. Olson, M. Cohen; A mechanism for the strain-induced nucleation of martensitic transformations, *Journal of the Less Common Metals*, 28(1) (1972) 107-118.
- [13] V.G. Gavriljuk, V.N. Shivanyuk, J. Foct; Diagnostic experimental results on the hydrogen embrittlement of austenitic steels, *Acta Materialia* 51 (2003) 1293-1305.
- [14] Z. Hua, D. Wang, Z. Liu, Y. Zhang, S. Zhu; Hydrogen distribution at twin boundary in austenitic stainless steel studied by scanning Kelvin probe force microscopy, *Materials Letters*, 234 (2019) 175-178.

- [15] M. Koyama, T. Ogawa, D. Yan, Y. Matsumoto, C.C. Tasan, K. Takai, K. Tsuzaki; Hydrogen desorption and cracking associated with martensitic transformation in Fe-Cr-Ni-based austenitic steels with different carbon contents. *International Journal of Hydrogen Energy* 42(2017) 26423-35.
- [16] L. Zhang, B. An, S. Fukuyama, T. Iijima, K. Yokogawa; Characterization of hydrogen-induced crack initiation in metastable austenitic stainless steels during deformation. *Journal of Applied Physics* 108 (2010) 063526.
- [17] J. Yamabe, O. Takakuwa, H. Matsunaga, H. Itoga, S. Matsuoka; Hydrogen diffusivity and tensile-ductility loss of solution treated austenitic stainless steels with external and internal hydrogen. *International Journal of Hydrogen Energy* 42 (2017) 13289-99.
- [18] Jr. C.J. McMahon; Hydrogen-induced intergranular fracture of steels. *Engineering Fracture Mechanics* 68 (2001) 773–88.
- [19] P. Novak, R. Yuan, B.P. Somerday, P. Sofronis, R.O. Ritchie; A statistical, physical-based, micro-mechanical model of hydrogen-induced intergranular fracture in steel, *Journal of the Mechanics and Physics of Solids* 58(2) (2010) 206-226.
- [20] CL. Lai, LW. Tsay, C. Chen; Effect of microstructure on hydrogen embrittlement of various stainless steels. *Materials Science & Engineering A* 584 (2013) 14-20.
- [21] M. Dadfarnia, B.p. Somerday, P.E. Schembri, P. Sofronis, J.W. Foulk, K.A. Nibur, D.K. Balch; On modeling hydrogen-induced crack propagation under sustained load, *JOM* 66(8) (2014) 1390-1398.
- [22] A. Traidia, E. Chatzidouros, M. Jouiad; Review of hydrogen-assisted cracking models for application to service lifetime prediction and challenges in the oil and gas industry, *Corrosion Reviews* 36(4) (2018) 323-347.
- [23] T.Y. Zhang, J.E. Hack; The equilibrium concentration of hydrogen atoms ahead of a mixed mode I-Mode III crack tip in single crystal iron, *Metallurgical and Materials Transactions A* 30(1) (1999) 155-159.
- [24] J. Lian, M. Sharaf, F. Archie, S. Münstermann; A hybrid approach for modelling of plasticity and failure behaviour of advanced high-strength steel sheets, *International Journal of Damage Mechanics* 22(2) (2013) 188-218.
- [25] J. Lian, P. Liu, S. Münstermann; Modeling of damage and failure of dual phase steel in Nakajima test, *Key Engineering Materials* 525-526 (2012) 69-72.
- [26] J. Talonen, P. Aspegren, H. Hanninen; Comparison of different methods for measuring strain induced α' -martensite content in austenitic steels, *Materials Science and Technology* 20(12) (2004) 1506-1512.
- [27] J. Lian, J. Wu, S. Münstermann; Evaluation of the cold formability of high-strength low-alloy steel plates with the modified Bai-Wierzbicki damage model, *International Journal of Damage Mechanics* 24(3) (2015) 383-417.
- [28] Y.F. Shen, X.X. Li, X. Sun, Y.D. Wang, L. Zuo; Twinning and martensite in a 304 austenitic stainless steel, *Materials Science and Engineering A* 552 (2012) 514– 522.
- [29] L.E. Murr, K.P. Staudhammer, S. S. Hecker; Effects of strain state and strain rate on Deformation-Induced Transformation in 304 Stainless Steel: Part II. Microstructural Study, *Metallurgical Transactions A*, 13 (1982) 627-635.
- [30] J. A. Venables; The martensite transformation in stainless steel, *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, 73(7) (1962) 35-44.
- [31] Y.O. K Nohara, N Ohashi; Composition and grain size dependencies of strain-induced martensitic transformation in metastable austenitic stainless steels, *ISIJ International* 63(5) (1977) 772-782.
- [32] A.M. Beese, D. Mohr; Effect of stress triaxiality and Lode angle on the kinetics of strain-induced austenite-to-martensite transformation, *Acta Materialia* 59(7) (2011) 2589-2600.

- [33] A.A. Lebedev, V.V. Kosarchuk; Influence of phase transformations on the mechanical properties of austenitic stainless steels, *International Journal of Plasticity* 16(7) (2000) 749-767.
- [34] C. San Marchi, B.P. Somerday, X. Tang, G.H. Schiroky; Effects of alloy composition and strain hardening on tensile fracture of hydrogen-precharged type 316 stainless steels, *International Journal of Hydrogen Energy* 33(2) (2008) 889-904.
- [35] D. Sun, G. Han, S. Vaodee, S. Fukuyama, K. Yokogawa; Tensile behaviour of type 304 austenitic stainless steels in hydrogen atmosphere at low temperatures, *Materials Science and Technology*, 17(3) (2001), 302-308.
- [36] T.C. Chen, S.T. Chen, W. Kai, L.W. Tsay; The effect of phase transformation in the plastic zone on the hydrogen-assisted fatigue crack growth of 301 stainless steel, *Materials Characterization* 112 (2016) 134–141.
- [37] C. Pan, W.Y. Chu, Z.B. Li, D.T. Liang, Y.J. Su, K.W. Gao, L.J. Qiao; Hydrogen embrittlement induced by atomic hydrogen and hydrogen induced martensite in type 304L stainless steel, *Materials Science and Engineering A351* (2003) 293-298.