Enhanced Resistance to Delayed Cracking in Deep-drawn Lean Duplex Stainless Steel: the Role of Residual Stress

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Abstract

The delayed cracking behavior of deep-drawn lean duplex stainless steel (LDSS) was investigated, and compared with that of conventional metastable austenitic stainless steels (MASS). Hydrogen charging was performed by electrochemical method, and the hydrogen charged specimens were subjected to the slow strain rate test. Fractures occurred along the phase boundaries in the LDSS, whereas the MASS specimens showed typical intergranular fractures after the hydrogen charging. In particular, the LDSS exhibited a superior limiting drawing ratio in spite of the large amount of internal hydrogen, and high sensitivity to hydrogen embrittlement. The high resistance to delayed cracking originated with the relatively lower residual stress generated during the deep drawing process. This is a
consequence of the suppression of martensitic transformation in the LDSS, due to Mn partitioning.

(Received January 18, 2017; Accepted March 27, 2017)

Keywords: delayed cracking, stainless steel, hydrogen, residual stress, martensite

1. INTRODUCTION

Duplex stainless steel is characterized by the ferrite-austenite dual-phase structure. Lean duplex stainless steel (LDSS) is one of three variants of duplex stainless steels, based on the pitting resistance equivalent number [1]. LDSS possesses high corrosion resistance and good mechanical properties for industrial applications. Moreover, the low amount of expensive alloying elements (e.g., Ni and Mo) also gives LDSS good price competitiveness [2]. These steels have recently attracted attention as an alternative to austenitic stainless steels, which are presently the most widely used type of stainless steels in the offshore plant industry [3].

Delayed cracking is the condition in which a fracture occurs after an incubation period of several minutes to days after the initial deformation. In structural materials this phenomenon must be avoided, as it may lead to catastrophic failure. A number of studies have suggested that there is a close relationship between delayed cracking and hydrogen embrittlement [4-7]. Previous researchers have investigated the hydrogen properties of deep-drawn cups to understand delayed cracking, because the deep drawing stress is closer to the actual stress state applied in the industry, as compared with a uniaxial deformation. For example, Papula et al. [8] revealed the influence of residual stress, strain-induced martensite, and internal hydrogen on the delayed cracking of deep-drawn metastable austenitic stainless steels (MASS). Berrahmoune, et al. [9] concluded that delayed cracking occurred at a high residual-stress level by tracking the amount and distribution of residual stress in a deep-
drawn austenitic steel cup.

Although many studies have investigated the fracture and corrosion behaviors of LDSS [1-3, 10], few researchers have focused on the delayed cracking phenomenon in this alloy. In particular, few studies have been conducted to observe the delayed cracking behavior in LDSS under the multi-axial stress conditions produced by deep drawing. In light of this, the present study investigated the delayed cracking phenomenon in deep-drawn LDSS cups. Improved resistance to delayed cracking in the LDSS is discussed in comparison to that of conventional MASS counterparts.

2. EXPERIMENTAL PROCEDURES

Three stainless steels were manufactured by POSCO for this work: a developed LDSS and two conventional MASS specimens following the AISI Type 200 standard (namely MASS-1 and MASS-2). Table 1 summarizes the chemical compositions of these steels. All of the steel plates were cold-rolled to a thickness of 1.2 mm, and then finally annealed at 1373 K for 30 s followed by air-cooling.

Deep drawing testing was performed using a universal sheet-metal test machine produced by J.T. Tohsi Inc. The machine was capable of pressing with a maximum punch power of 50 tons, with a punch stroke of 200 mm, and a punch speed of 500~600 mm/min. Wire-cut circular specimens were lubricated with tallow oil, and then deep-drawn using a flat-type cylindrical punch at a punch speed of 100 mm·min⁻¹ under a holding force of 10 kN. A digital camcorder was incorporated to measure the precise time elapsed before crack initiation. The drawing ratio (DR) was determined from the ratio of the initial diameter of the circular specimen (75-102 mm) to the punch diameter (50 mm).

For further investigations, hydrogen was driven into a section of the specimens using an aqueous solution of 0.4% NH₄SCN and 4% NaCl, at various current densities between
0.085-30 A·m⁻². All specimens were mechanically polished with #1200-grit abrasive paper before the hydrogen charging to ensure uniform surfaces. The charging temperature was set to be a constant 360 K using a heating mantle. The slow-strain-rate test (SSRT) was conducted at a strain rate of 5 × 10⁻⁵ s⁻¹ at room temperature. SSRT samples were machined with a gauge width of 6 mm and a gauge length of 25 mm. The amount of hydrogen inside the material was measured using thermal desorption analysis (TDA). Samples were heated up to 673 K at a heating rate of 100 K·h⁻¹, during which the emitted gas was transferred to a gas chromatograph with He carrier gas, at 5-min intervals.

The initial microstructures prior to commencing the deep drawing were observed using the electron backscatter diffraction (EBSD) technique performed at 20 kV. For this purpose, the samples were mechanically polished with #2400-grit abrasive paper, and then electro-polished at 45 V in an etchant of 6 ml perchloric acid and 94 ml acetic acid. The fracture surfaces of the deep-drawn steels were observed using a field-emission scanning electron microscope (FE-SEM) at 10 kV. A ferrite scope was used to determine the volume fraction of strain-induced martensite. Electron probe micro-analysis (EPMA) was utilized to investigate the Mn distribution in the LDSS. The samples were mechanically polished with #2400-grit abrasive paper and colloidal silica to obtain a mirror surface.

Tangential residual stress formed in the wall of the deep-drawn cups was measured using a ring-slitting method [11] (Figure 1). The deep-drawn cup was sliced in the plane normal to the drawing direction in a water bath to prevent frictional heat, and then slitted to measure the diameter of a closed ring (D₀) and an opened ring (D₁). The change in wall thickness was determined to be negligible. Tangential residual stress (σ) was determined as follows: \( \sigma = E t \left[ \frac{1}{D_0} - \frac{1}{(D_0 + D_1)} \right] \) where \( E = 328 \) GPa for LDSS, 287 GPa for MASS-1, and 235 GPa for MASS-2, respectively) is the elastic modulus and \( t \) is a sample thickness. The top ring, as marked in red in Figure 1, was used for this measurement because cracking
3. RESULTS AND DISCUSSION

The initial microstructure of the investigated stainless steels was observed in a plane normal to the transverse direction (Figure 2). The LDSS exhibited a layered austenite-ferrite structure with an average grain size of 6.4 μm. The volume fraction of each phase was 34% for ferrite and 66% for austenite. MASS-1 and MASS-2 exhibited a single austenitic structure composed of larger equiaxed grains with sizes of 18.3 μm and 16.3 μm, respectively. Twins were confirmed in the austenite phase of all the stainless steels. The different microstructures gave rise to differences in yield stress (YS) and total elongation (TE) for the investigated steels (Figure 3). The LDSS exhibited a higher YS (549 MPa) and lower TE (43%) in comparison to MASS-1 (441 MPa and 58%) and MASS-2 (412 MPa and 57%). However, the ultimate tensile stress (UTS) of the investigated steels was comparable: 826 MPa for LDSS, 834 MPa for MASS-1, and 861 MPa for MASS-2. This suggests that the developed LDSS could be used as an alternative to the conventional MASS counterparts.

The investigated steels showed similar fracture surfaces after the tensile test, in which dimples indicated a ductile fracture. In contrast, there were significant differences between LDSS and the MASS counterparts in the fracture surfaces that were observed after the deep drawing (Figure 4). MASS-1 and MASS-2 showed a typical intergranular fracture. That phenomenon is a consequence of the reduction in grain-boundary strength produced by hydrogen segregation at the grain boundaries [12]. In the LDSS, however, it appears that the fracture occurred along the phase boundaries. The finer grains in the LDSS produce a higher fraction of grain boundaries, compared to the MASS counterparts. This increase in boundaries reduced the applied stress per unit grain boundary, and thus suppressed the intergranular fracture to some degree [13]. It assisted in producing the delayed cracking at the
phase boundaries in LDSS.

This work utilized the limiting drawing ratio (LDR) to evaluate the resistance to delayed cracking. The LDR was determined to have the highest DR when delayed cracking did not occur up to 100 h after the deep drawing process. The amount of internal hydrogen injected into the LDSS (0.84 mass ppm) was more than double the amount in MASS-1 (0.24 mass ppm) and MASS-2 (0.36 mass ppm) at the same current density. A significant amount of internal hydrogen generally gives rise to a deterioration in deep drawing formability [14].

Moreover, the LDSS exhibited a considerable decrease in tensile ductility in contrast to the MASS counterparts in SSRT, after charging with a similar amount of hydrogen (Figure 5). The reduction in elongation was calculated to be 79% for LDSS, in contrast to 31% for MASS-2. These results indicate that LDSS has a higher sensitivity to hydrogen embrittlement. This tendency originates with the ferrite in the LDSS: hydrogen diffusivity in ferrite is more than five-orders higher than in austenite [15,16]. It is very interesting, however, that the LDR of the LDSS (2.0) was higher than that of MASS-1 (1.6) and MASS-2 (1.7). Figure 6 shows delayed cracking in the deep-drawn steels, which were drawn with a draw ratio (DR) just above the LDR value of each steel. Therefore, the LDSS exhibited superior resistance to delayed cracking in spite of its higher amount of internal hydrogen and higher sensitivity to hydrogen embrittlement (i.e., a larger reduction in tensile elongation, as shown in Fig. 5).

The experimental results imply the existence of a primary factor, other than internal hydrogen, affecting the deep drawing formability. To elucidate such a factor, further investigation was performed with hydrogen-charged and then deep-drawn steels (Figure 7). None of the investigated steels experienced delayed cracking at a DR of 1.6, before the hydrogen charging. This is not surprising since the applied DR was lower than the LDRs of these steels, as noted above. It is of particular note, however, that the MASS specimens showed an obvious trend of delayed cracking after the hydrogen charging, whereas the LDSS
successfully inhibited the occurrence of delayed cracking under the same conditions. Increasing the DR from 1.6 to 2.0 finally induced the delayed cracking in the LDSS; note that this value was the LDR for the material before the hydrogen charging.

We then focused on the role of residual stress in the delayed-cracking resistance of a deep-drawn cup. Strong tangential residual stress can be developed in the wall of the deep-drawn cup due to inhomogeneous deformation and stress distribution during the deformation process. Increasing DR gives rise to an increase in martensitic fraction and tangential residual stress [17]. A previous work also indicated that residual stress was a fundamental cause of the delayed fracture of twinning-induced plasticity steel, using the neutron diffraction method [18].

Indeed, residual stress can explain most of the present results. Recalling Figure 7, the residual stress determined the degree of material deterioration. The crack incubation time, representing the resistance to delayed cracking, decreased with an increase in residual stress (427 MPa for LDSS, 735 MPa for MASS-1, and 541 MPa for MASS-2). It should also be noted that increased DR led to an increase in both martensitic volume fraction and tangential residual stress (Figure 8). The LDSS showed a markedly lower fraction of martensite compared to the MASS counterparts in the investigated DR range. The hard martensitic phase constrains neighboring phases during deformation, resulting in increased residual stress [8]. Hence, residual stress should be considered the primary factor when interpreting the delayed-cracking behaviors of the investigated steels. The relatively suppressed formation of strain-induced martensite in the developed LDSS contributed to a decrease in residual stress, and a corresponding improvement in resistance to the delayed cracking.

The low fraction of martensite in the LDSS can be explained in terms of the partitioning of Mn, which acts as an austenite stabilizer. EPMA analysis was used to determine the Mn concentration of the austenitic phase in the developed LDSS (Figure 9).
The quantitative measurement revealed that the austenitic phase possessed a 0.95 wt% higher amount of Mn on average than the ferritic phase in the developed LDSS. Considering the austenite-stabilizing affect of Mn, this assisted in the suppression of the martensitic transformation. The partitioning effect occurred only in the LDSS, since the MASS counterparts were composed of a single-phase structure.

The interpretation suggested in this work also well explains why the hydrogen-charged MASS-1 exhibited the lowest resistance to delayed cracking, as shown in Figure 7. Comparing the two MASS specimens, MASS-1 contained a lower amount of Ni, which also acts as an austenite stabilizer [19]. This led to an accelerated martensitic transformation during deformation, as characterized by the higher martensitic fraction at the same DR in Figure 8, resulting in significant residual stress. For example, the tangential residual stress of MASS-1 was 735 MPa at a DR of 1.6, while that of MASS-2 was 541 MPa. The excessive residual stress resulted in the deterioration of the delayed-cracking resistance of MASS-1.

4. CONCLUSIONS

This study clarified the enhanced resistance to delayed cracking of the deep-drawn LDSS material. The mechanisms behind this improvement were discussed, in comparison to two conventional MASS specimens.

(1) The LDSS contained a ferrite-austenite dual-phase structure, while the MASS samples were composed of a single austenite. The LDSS exhibited a higher YS and lower TE compared to the MASS counterparts. Nevertheless, the LDSS is expected to replace MASS specimens, as their UTS values were comparable.

(2) The hydrogen charging induced a typical intergranular fracture in the MASS specimens. In contrast, in the LDSS, the fracture occurred along the phase boundaries due to its higher fraction of grain boundaries, which reduced the applied stress per unit boundary.
The LDSS exhibited superior resistance to delayed cracking in spite of its higher amount of internal hydrogen, and higher sensitivity to hydrogen embrittlement (i.e., a larger reduction in tensile elongation). The residual stress was the primary factor governing the delayed-cracking resistance of the investigated steels.

(3) The partitioning of Mn elements can assist in suppressing the transformation of austenite into martensite in the developed LDSS. The low amount of Ni led to the high fraction of the strain-induced martensite, and the considerable residual stress in MASS-1, resulting in the lower resistance to delayed-cracking.

Acknowledgement

The authors gratefully acknowledge that POSCO supported this research.
REFERENCES

17 X. Guo, J. Post, M. Groen, and W. Bleck, Steel Res. Int. 82, 6 (2011).


Table and figures

**Table 1** Chemical composition of the investigated materials (unit: mass percent)

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Si</th>
<th>Cr</th>
<th>N</th>
<th>Fe</th>
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<tbody>
<tr>
<td>LDSS</td>
<td>0.1</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>20</td>
<td>0.17</td>
<td>Bal.</td>
</tr>
<tr>
<td>MASS-1</td>
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<td>1</td>
<td>1.5</td>
<td>0.5</td>
<td>16</td>
<td>0.2</td>
<td>Bal.</td>
</tr>
<tr>
<td>MASS-2</td>
<td>0.07</td>
<td>5.5</td>
<td>3.6</td>
<td>0.3</td>
<td>0.5</td>
<td>18</td>
<td>0.17</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

**Fig. 1** Schematic diagram showing the ring-slitting method composed of deep-drawing, slicing, and slitting steps.
Fig. 2 Initial microstructures of the investigated steels obtained by EBSD analysis: (a) LDSS, (b) MASS-1, and (c) MASS-2. Phase map of MASS specimens was not presented as the alloys consist of a single austenitic phase.

Fig. 3 Engineering stress-strain curves of the investigated steels before the deep drawing.
Fig. 4 Fracture surfaces obtained after the deep drawing of (a) LDSS (DR = 2.0) and (b) MASS-2 (DR = 1.8).

Fig. 5 SSRT curves obtained before and after the hydrogen charging: (a) LDSS and (b) MASS-2. Note that a similar amount of hydrogen was charged in each material: 28 mass ppm and 25 mass ppm, respectively.
**Fig. 6** Delayed cracking observed in the deep-drawn steels which were drawn with the draw ratio (DR) just above the LDR of each steel.

**Fig. 7** Crack incubation time for delayed cracking of hydrogen-charged and deep-drawn steels. The data points at 100 h indicate that the material did not fracture up to this incubation time.
**Fig. 8** Tangential residual stresses determined at the top ring of deep-drawn cups with various DR values in relation to martensitic fraction. The black line was drawn by numerically fitting the data.

**Fig. 9** EPMA line profile for Mn concentration in LDSS. ‘F’ and ‘A’ indicate the ferrite and austenite, respectively.