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The effect of Zn coating layers on the hydrogen embrittlement of hot-dip galvanized twinning-induced plasticity steel

Hyun-Hee Jeon[a], Sang-Min Lee[a], Jeongho Han[a,b], Il-Jeong Park[a,c], Young-Kook Lee[a,*]

[a] *Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea*
[b] *Current affiliation: Department of Microstructure Physics and Alloy Design, Max-Planck-Institut für Eisenforschung, Düsseldorf 40237, Germany*
[c] *Current affiliation: Surface Technology Research Group, POSCO, Gwangyang 57807, Republic of Korea*

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ABSTRACT

The effect of Zn coating layers on hydrogen embrittlement (HE) was investigated using hot-dip galvanized (HDG) twinning-induced plasticity (TWIP) steel. The Zn coating layers consisted of an η-Zn layer and Fe-Zn intermetallic layers of ζ and δ without Γ. H was trapped particularly at the ζ layer without Zn-H compounds. The activation energies of H desorption from the δ and ζ layers were 60.0 kJ mol^{-1} and 75.4 kJ mol^{-1}, respectively. The H-charged HDG_TWIP steel did not reveal HE due to the intermetallic layers, which are exceptionally brittle even when H is not enriched.

1. Introduction

Fe-Mn-C ternary twinning-induced plasticity (TWIP) steels have been extensively studied with the expectation of next-generation automotive steels due to their excellent combination of high strength (>800 MPa) and high ductility (>60%) [1–4]. Mechanical twins forming during plastic deformation reduce the effective grain size of austenite (γ) and act as obstacles to the gliding of dislocations. This dynamic Hall-Petch effect [5] raises the strain hardening rate (SHR), resulting in remarkable mechanical properties [6,7].

The resistance to hydrogen embrittlement (HE) of TWIP steels also has been actively investigated due to the vulnerability of high strength steels of over ~1 GPa to HE [8–10]. For example, when TWIP steel is exposed to a corrosive environment, H permeates the steel by the hydrogen evolution reaction (HER) [11–13]. Once H is introduced to the TWIP steel, the intersections of twin–twin and twin-grain boundaries are enriched with H and act as crack initiation sites, causing premature brittle fracture [14,15]. However, fortunately, when Fe-Mn-C ternary TWIP steel is supplemented with Al [16–18] and/or grain-refined [19,20], the resistance to HE is improved primarily due to the reduction of twin density.

Meanwhile, we believe that hot-dip galvanizing (HDG), which is performed for better corrosion resistance [21], can also improve the resistance to HE, considering that the pure Zn (η-Zn) layer suppresses the permeation of H into the steel [22,23]. This by-effect of HDG is a result of the low exchange current density for the HER of η-Zn [24,25] reducing the concentration of dissolved H at the specimen surface and/or because a Zn passive film ($Zn(OH)_2$) forms at the surface by corrosion [23] to suppress the HER [26]. However, once H enters the Zn coating layers, including the η-Zn layer and Fe-Zn intermetallic layers such as ζ, δ and Γ layers, it easily diffuses inside the η-Zn layer due to its high diffusivity in Zn at room temperature (RT) (~10^{-8} m^2 s^{-1} [27]), which is greater than that of H in *fcc* γ-austenitic steel (~10^{-15} m^2 s^{-1} [28]). H-charged η-Zn exhibited a substantial decrease of elongation due to both the formation of a brittle Zn hydride (ZnH_2) and the dislocation pinning effect of H [29].

Accordingly, it is still ambiguous how much the η-Zn layer contributes to the improvement of the resistance to HE. In addition, in the case of steels hot-dip galvanized in a pure Zn bath, besides the η-Zn layer, various Fe-Zn intermetallic layers of ζ, δ, and Γ form [30]. Although the intermetallic layers are known to be mechanically brittle [31,32], there have been few reports on the intermetallic layers of TWIP steel hot-dip galvanized in a pure Zn bath and their effect on HE. Upon this background, the objective of the present study is to investigate the effect of the Zn coating layers including the intermetallic layers on the HE of hot-dip galvanized Al-bearing

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[*] Corresponding author.
E-mail address: yklee@yonsei.ac.kr (Y.-K. Lee).

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TWIP steel, viz. the strong trapping layer of the permeated H, the activation energy of H desorption from the intermetallic layers, and the crack initiation layer.

2. Experimental procedure

A $\sim$20 kg ingot of Fe-18Mn-0.6C-2Al (wt.%) was cast using a vacuum induction furnace. The accurate chemical composition of the ingot was Fe-18.02Mn-0.59C-1.9Al-0.019P-0.012S in weight percent. The ingot was solution-treated at 1473 K for 1.5 h, hot-rolled at $\sim$1173 K to a 3-mm-thick plate, held at 773 K for 1 h, and then air-cooled to RT for a coiling simulation. The hot-rolled plate was cold-rolled to a 1.5-mm-thick sheet after surface descaling, corresponding to a thickness reduction of 50%. The cold-rolled specimens were annealed at 1273 K for 10 min for recrystallization using a vacuum tubular furnace, followed by water quenching to RT.

The annealed specimens were mechanically polished using a 1-μm diamond suspension, hot-dip galvanized for 30 s in a molten Zn bath held at 723 K, followed by air cooling to RT. The purity of Zn was 99.995 wt.%. Some of the hot-dip galvanized TWIP specimens were annealed at 823 K for 4 min using a vacuum tubular furnace. Hereafter, the annealed, hot-dip galvanized, and hot-dip galvanized and annealed specimens are denoted as TWIP, HDG_TWIP, and annealed HDG_TWIP, respectively.

The microstructures of the three types of TWIP specimens were observed using an optical microscope (OM; Olympus, BX41M) and a field-emission scanning electron microscope (FE-SEM; JEOL, JSM-7001F) equipped with an electron backscattered diffractometer (EBSD; EDAX-TSL, Digiview). The specimens for OM, SEM, and EBSD were prepared using a hot mounting press (Struers, CitoPress-5) at 453 K under a pressure of 325 MPa. The mounted specimens were polished using an auto polisher (Struers, LectroPol-5) with a 1-μm diamond suspension, and then chemically etched using a 4% nital solution. The EBSD specimen was polished with a 0.04-μm colloidal silica suspension. The accelerating voltage, probe current, working distance, and step size for EBSD operation were 20 kV, 12 nA, 15 mm, and 60 μm, respectively. The TWIP specimen had a γ-austenitic single phase, as was expected. The average grain size of γ-austenite was $\sim$35 μm, which was measured by the linear intercept method including annealing twin boundaries.

The constituent phases in the three types of TWIP specimens were examined using an X-ray diffractometer (XRD; RIGAKU, D/MAX-RINT 2700) with a Cu target ($\lambda = 1.5405$ Å). The scanning range, rate, and step size were 20°–100°, 2° min^{-1}, and 0.02°, respectively. The chemical composition of each phase was examined using a field-emission gun electron probe microanalyzer (FEG-EPMA; JEOL, JXA-8500F). The operating voltage, probe current, and spatial resolution were 15 kV, 15 nA, and 1 μm, respectively. The XRD and EPMA specimens were prepared by the same method as employed for the OM specimens.

Tensile specimens were machined to the ASTM E8M-04 subsize along the cold rolling direction. The gauge part of the tensile specimens was 6 mm in width, 25 mm in length, and 1.5 mm in thickness. Slow strain rate tensile tests (SSRT) were conducted with both H-uncharged and charged specimens using a servo hydraulic universal tensile testing machine (Instron, 3382) at a crosshead speed of 0.1 mm min^{-1}, corresponding to an initial strain rate of 4.8×10^{-5} s^{-1}.

Tensile specimens were cathodically charged with H in a 3% NaCl aqueous solution containing 0.3% NH_4SCN according to ISO 16573. The current density, charging time, and temperature were 50 A m^{-2}, 48 h, and 300 K, respectively. NaCl is dissolved to Na^+ and Cl^- ions in the aqueous solution to act as electrolytes; NH_4SCN acts as an inhibitor to the recombination of H^+ ions into a gaseous form during H charging. The H concentrations of the H-charged specimens were converted from the H desorption rate curves measured by a thermal desorption analysis (TDA) during continuous heating of the H-charged specimens at 373 K h^{-1} from 300 K to 700 K [33]. A pulsed discharge ionization detector (PDID) for TDA has a sensitivity ranging from 10^{-5} ppb to 10^{-8} ppb, considering the mass of each specimen used. Both TDA and SSRT were promptly performed within $\sim$3 min after H charging.

Table 1
Fe concentration and average thickness of each coating layer in the HDG_TWIP specimen.

Layer	Fe concentration (wt.%)			Layer thickness (μm)
	Present study	References		
η	0.2–0.3	0–0.03 [30]	0.3–0.4 [23]	60
ζ	5.2–6.1	5.0–6.0 [30]	5.0–6.1 [35]	26
δ	8.6–10.7	7.0–11.5 [30]	6.9–11.4 [35]	4

3. Results and discussion

Figs. 1a and b show FE-SEM micrographs of the HDG_TWIP specimen, taken from the transverse direction (TD). At a low magnification, two layers appear to form at the surface of the TWIP steel (Fig. 1a); the outer layer with an average thickness of 60 μm was assumed to be a η-Zn layer and the inner layer with an average thickness of 30 μm an Fe-Zn intermetallic layer. However, when the Zn coating layers were magnified (a yellow solid box in Fig. 1a), three different layers were observed, as another thin intermetallic layer appeared just above the matrix (Fig. 1b).

According to previous studies [30,34,35], four different Zn coating layers form in the following order from the matrix; Γ, δ, ζ, and η layers. The η-Zn layer is the pure Zn phase and the other layers are Fe-Zn intermetallic phases. The Fe concentration within the intermetallic layers decreases in the order of Γ, δ, and ζ. Therefore, to identify the three layers (Fig. 1b), an XRD test was performed at the normal direction (ND) of the surface of the HDG_TWIP specimen. Whereas the XRD peaks of the η-Zn phase, ζ- and δ-intermetallic phases were observed, the peaks of the Γ-intermetallic phase and the γ-austenitic matrix were not observed (Fig. 1c). The absence of the Γ phase is most likely due to a short dipping time of 30 s, considering that whereas both the ζ and δ phases form even after a short dipping time $\sim$5 s [30], the formation of the Γ phase demands a relatively long dipping time [30,34]. The absence of the peaks of the γ-austenitic matrix implies that the X-ray radiation did not reach the matrix through the $\sim$90-μm-thick Zn coating layers.

Comprehensive analyses of SEM images (Fig. 1b), XRD peaks (Fig. 1c), and previous reports on the formation order of intermetallic layers indicate that the outmost coating layer is the η-Zn phase, the middle layer is the ζ phase, and the bottom layer is the δ phase in Fig. 1b. To reconfirm the constituent phases of the Zn coating layers, the Fe concentration of each layer was measured more than three times using SEM-EPMA, and compared with that reported in the literature. The η-Zn, ζ, and δ layers contained (0.2–0.3 wt.%) Fe, (5.2–6.1 wt.%) Fe, and (8.6–10.7 wt.%) Fe, respectively; these values match well with reported Fe concentrations of the three layers [23,30,35], as listed in Table 1.

Meanwhile, as shown in Fig. 1b, the ζ layer is thicker than the δ layer; this is most likely due to the high carbon concentration (0.6 wt.%) of the present TWIP steel, considering a previous report that when the C concentration of the matrix is higher than $\sim$0.3 wt.%, the growth rate of the ζ layer rapidly increases due to an active dissolution reaction of Fe into Zn [36]. The SEM-EPMA tests of the ζ layer exhibited that a small amount of the η-Zn phase with (0.1–0.3 wt.%) Fe is embedded between the columnar grains of the ζ phase (Fig. 1b).