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The mechanism of hydrogen embrittlement in intercritically annealed medium Mn TRIP steel

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ABSTRACT

The objective of this study was to investigate the mechanisms of hydrogen embrittlement (HE) in intercritically annealed medium Mn steel. For this purpose, both hot-rolled and cold-rolled Fe-7Mn-0.1C-0.55Si (wt.%) steels were annealed at 640 °C for 30 min. The annealed specimens had a dual-phase microstructure of retained austenite (γR) and ferrite (α) with different morphologies; a lath shape for the hot-rolled and annealed (HRA) specimen and a globular shape for the cold-rolled and annealed (CRA) specimen. Although the difference in microstructural morphology did not influence the H permeation, it significantly affected the HE behavior. The H-charged HRA (HRAH) specimen was fractured by intergranular cracking occurring along the boundaries of prior γ grains by the H-enhanced decohesion (HEDE) mechanism. The intergranular cracking left both flat and rugged facets, which appeared at the prior γ grain boundaries without and with γR, respectively. The H-charged CRA (CRAH) specimen was fractured to leave both dimples filled with grains and empty dimples at the fractured surface. The dimples filled with grains were generated by intergranular cracking occurring along the boundaries of γR grains by the HEDE mechanism. The empty dimples were made by intragranular cracking occurring inside the α grains by the H-enhanced local plasticity (HELP) mechanism. The CRAH specimen exhibited a smaller elongation loss than the HRAH specimen because cracks were propagated by frequently changing their direction along the boundaries of nano-sized γR grains or into α grains.

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1. Introduction

In recent, medium Mn transformation-induced plasticity (TRIP) steel with 3–10 wt% Mn has been received significant attention as advanced high strength steel due to its excellent mechanical properties and reasonable materials cost [1–16]. Most of studies on medium Mn TRIP steels [1–16] focused on the effects of alloying elements and intercritical annealing conditions, such as annealing temperature [2,3], annealing time [4,5], heating rate [6] and cooling rate [7], on the microstructure and mechanical properties.

Briefly speaking of previous results, medium Mn TRIP steels normally exhibit an α′ martensite microstructure after hot and cold rolling and a dual-phase microstructure consisting of ultralight-grained α ferrite and retained austenite (γR) after intercritical annealing [1]. The volume fraction of γR in intercritically annealed medium Mn TRIP steels ranges from ~0.2 to 0.4, which is greater than that in conventional TRIP steels with less than 3 wt%Mn (~0.15) [17,18]. Both the ultralight grain size and the active TRIP occurring in the large fraction of γR result in a remarkable combination of tensile strength (max. 1300 MPa), total elongation (max. 40%) [1–13] and high impact toughness (~250 J cm⁻² at room temperature) [14–16].

However, regarding the H embrittlement (HE), there are only a couple of articles [19,20] till now, although it is well-known that high strength steels with tensile strengths of over 1.0 GPa are vulnerable to the HE [21]. Ryu et al. [19] reported that γR more strongly traps H compared to α and α′ martensite in cold-rolled and annealed Fe-4.6Mn-0.12C-0.55Si-1.1Al and Fe-5.8Mn-0.12C-0.47Si-3.1Al (wt.%) steels. They claimed that H was inherited from γR to α′ martensite by deformation-induced transformation and that the inherited H deteriorated the ductility of the TRIP-assisted steels because the diffusivity of H in α′ martensite is greater than that in γR [19].

Wang et al. [20] examined the resistance to HE in both as-hot-rolled and hot-rolled and intercritically-annealed Fe-9Mn-0.01C-

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3Ni-1.4Al (wt.%) steel. Whereas the as-hot-rolled specimen had fully y martensite, the intercritically-annealed specimen possessed a dual-phase microstructure consisting of -65% z and -35% γR in volume percent. The annealed steel showed a higher resistance to HE than the as-hot-rolled steel because γR has a lower diffusivity and a higher solubility of H than z martensite. They directly observed that deformation-induced z martensitic transformation in the nano-films of γR triggered cracking in a H-charged medium Mn TRIP steel; this matches well with the result reported by Ryu et al. [19]. However, aforementioned two reports did not explain detailed HE mechanisms of medium Mn TRIP steel, such as internal pressure model [22,23], H-enhanced decohesion (HEDE) [24,25] and H-enhanced local plasticity (HELP) [26–28].

Meanwhile, considering above two reports in a viewpoint of microstructural morphology, whereas Ryu et al. [19] examined the HE of the cold-rolled and annealed steel with a globular-shaped microstructure, Wang et al. [20] studied the HE of the hot-rolled and annealed steel with a lath-shaped microstructure. It is known that the microstructural morphology of annealed medium Mn steels changes from the lath shape to the globular shape by cold-rolling [1]. The difference in microstructural morphology influences the yielding behavior; whereas the hot-rolled and annealed specimen exhibited continuous yielding, the cold-rolled and annealed specimen showed discontinuous yielding and a large yield point elongation [1]. However, there is no report yet on the effect of the difference in morphology between the hot-rolled and cold-rolled specimens on the formation and propagation of H-induced cracks.

Therefore, in the present study we prepared medium Mn TRIP steel specimens with the lath-shaped microstructure by hot rolling and annealing and with the globular-shaped microstructure by cold rolling and annealing, and comparatively investigated the HE mechanisms in the specimens with different microstructural morphologies but the same chemical composition.

2. Experimental procedure

A 30 kg ingot of Fe-7Mn-0.1C-0.5Si (wt.%) steel was cast using a vacuum induction furnace. The actual chemical composition of the ingot was Fe-7.22Mn-0.093C-0.49Si-0.013Al-0.005P-0.007S in weight percent. The ingot was homogenized at 1150 °C for 12 h, hot-rolled to ~3-mm-thick plate at temperatures ranging from ~1100 °C to 900 °C, and then air-cooled to room temperature. A part of the hot-rolled plate was cold-rolled with a thickness reduction of ~55% after surface descaling.

Both the hot- (HR) and cold-rolled (CR) specimens were intercritically annealed at 640 °C for 30 min in a vacuum atmosphere using a tubular furnace, and then air-cooled to room temperature. Hereafter, the HR and annealed specimen is called the HRA specimen and the CR and annealed specimen is called the CRA specimen. The annealing temperature was determined as a mid-temperature between equilibrium eutectoid (Ae1) and ferrite start temperature between equilibrium eutectoid (Ae1) and ferrite start temperature (CF). The annealing temperature was determined as a mid-

The volume fraction of γR in the annealed specimens used for SEM and EBSD observation were determined using a high-resolution X-ray diffractometer (XRD; RIGAKU, SmartLab) with a Cu-Kα radiation (λ = 1.5405 Å). The scanning range, rate and step size were 40°–100°, 2° min⁻¹ and 0.02°, respectively. The volume fraction of γR was determined using the integrated intensities of all diffractions peaks [30]; the lattice parameter of γR was determined by the Nelson-Riley method [30].

The sub-sized tensile specimens (ASTM EBM-04) were machined along the rolling direction. The thickness, width and length of the gauge portion were 1.25 mm, 60 mm and 25 mm, respectively. Tensile tests were conducted with a slow strain rate of 1 × 10⁻⁴ s⁻¹ at room temperature before and after H charging using an Instron 3382 machine. The H-charged specimen was tensile-strained within 5 min after H charging. Tensile specimens were electrochemically H-charged in an aqueous solution of 3 wt% NaCl and 0.3 wt% NaHSO₃ with a current density of 50 A m⁻² at room temperature for 3 h using a Pt wire as a counter-electrode. The charging time (t₁) of 3 h was determined to fully charge the 1.25-mm-thick tensile specimen based on a diffusion distance of H ([D_Η]t₁/₂), where [D_Η] is an effective diffusion coefficient of H at room temperature in low alloy martensitic steel ([D_Η] = 3.70 × 10⁻¹⁰ m² s⁻¹) [31]. To measure the concentrations of diffusible H in the H-charged specimens, thermal desorption analyses (TDA) of the H-charged tensile specimens were conducted using a gas chromatography system (Agilent Technologies 7890A) and a tubular furnace in a He gaseous atmosphere. The TDA was conducted within 10 min after H charging. During continuous heating from room temperature to 300 °C at a rate of 100 °C h⁻¹, the amount of the H gas released from the H-charged specimen was analyzed with an interval of 5 min using He as a carrier gas.

3. Results and discussion

Fig. 1a shows an EBSD inverse pole figure (IPF) map of the HR specimen. The white lines are the high-angle boundaries of prior γ grains with the misorientation angles of 20°–50° [32]. Each prior γ grain is composed of several packets and blocks with different orientations; this indicates that the HR specimen has a martensitic microstructure, as was expected. An average size of prior γ grains was ~35 μm. To confirm the presence of γR in the HR and CR specimens, XRD tests were performed. Both specimens exhibited diffraction peaks of only a bcc phase, as shown in Fig. 1b. This indicates that both specimens had a single z martensitic microstructure without γR.

Fig. 2a provides dilatometric curves of both HR and CR specimens measured during intercritical annealing at 640 °C for 30 min and during gas quenching. Both specimens showed the reduction in strain during holding at 640 °C, which was caused by the reverse transformation from z martensite to γ. Considering the fact that there was no change in slope of dilatometric curves measured
during quenching, it is thought that αʹ martensitic transformation did not occur during quenching. This indicates that the reverted γ at 640 °C fully remained at room temperature after quenching as the γR.

To measure the volume fraction of γR after intercritical annealing, XRD tests were performed using the dilatometric specimens annealed at 640 °C for 30 min (Fig. 2b). The annealed specimens distinctly showed the diffraction peaks of an fcc phase as well as a bcc phase; this is indicative of the presence of γR, which formed by the reverse transformation from αʹ martensite to γ during annealing.

The volume fractions of γR in the HRA and CRA specimens were ~0.47 and 0.50, respectively. The equilibrium volume fraction of γ at 640 °C, which was calculated by Thermo-Calc software with TCFE 7 database [29], was ~0.59. Accordingly, it was realized that the actual volume fraction of γ reverted during annealing at 640 °C for 30 min did not reach the equilibrium volume fraction of γ yet.

To examine the difference in microstructural morphology between the HRA specimen and the CRA specimen, EBSD observation was conducted (Fig. 3). The HRA specimen had a dual-phase microstructure of lath-shaped α (αL, red) and γR (γL, green), as shown in an EBSD IQ-phase map (Fig. 3a) because the reverted γ grew along the boundaries of martensite blocks occurred prior to the recrystallization of the αʹ martensite matrix [1]. The widths of both αL and γL were ~300 nm and 260 nm, respectively. The CRA specimen had a dual-phase microstructure of globular-shaped α (αG) and γR (γG), as shown in an EBSD IQ-phase map (Fig. 3b) because the recrystallization of the αʹ martensite matrix took place prior to the reverse transformation from αʹ martensite to γ [1]. The average grain sizes of αG and γG were ~450 nm.

To investigate the partitioning behavior of alloying elements, such as C and Mn, between α and γ phases during intercritical annealing, TEM-EDXS analyses were performed on the grains marked in the TEM micrographs of both HRA and CRA specimens (Fig. 4a and b). The average Mn concentrations of αL and γL in the HRA specimen (Fig. 4a) were ~3.9 wt% and 10.3 wt% (Fig. 4c); those of αG and γG in the CRA specimen (Fig. 4b) were ~3.6 wt% and 10.1 wt% (Fig. 4c). The equilibrium Mn concentrations of α and γ at 640 °C, which were calculated by Thermo-Calc software with TCFE 7 database [29], was 2.8 wt% and 10.2 wt%, respectively. It is thought that the difference between measured and equilibrium Mn concentrations is most likely due to the instrumental error of TEM-EDXS.

Meanwhile, the C concentrations of both γL and γG were calculated using the following equation [33]:

$$a_\gamma = 3.5780 + 0.033C + 0.00095Mn$$  (1)

where $a_\gamma$ is a lattice parameter of γR at room temperature (Å), C and
The concentrations of Mn and C in ferrite and retained austenite phases. Underwent TDA at a heating rate of 100°C/min and TWIP steel were electrochemically H-charged for 48 h, and this result indicates that the H desorption rate peaks of HRAH and CRAH specimens with ~50% full austenitic TWIP steel. This is because both αf and Mn concentration had the measurement errors and the actual volume fraction of reverted γ was less than the equilibrium volume fraction of γ.

To investigate the HE behavior of HRA and CRA steels with different microstructural morphologies, at first the H-charged HRA (HRAH) and CRA (CRAH) tensile specimens underwent the TDA before slow strain rate tensile tests (SSRT). TDA was conducted twice per each specimen during continuous heating from room temperature to 300°C at a rate of 100°C/h (Fig. 4a). Both HRAH and CRAH specimens exhibited a peak ranging from room temperature to ~200°C; a maximum H desorption rate appeared at ~80°C. The TDA curves match well with those reported previously [19,20]. The concentration of diffusible H was converted from the peak to be ~1.2 mass ppm in both HRAH and CRAH specimens.

For in-depth analysis of the H desorption rate peak, the TDA curves of a medium Mn steel (Fe-5.8Mn-0.1C-3.1Al-0.5Si (wt.%)) with a dual-phase microstructure of α and α′ martensite without γR [19] and a full austenitic twinning-induced plasticity (TWIP) (Fe-18Mn-0.6C (wt.%)) steel [34] are plotted together with those of present HRAH and CRAH specimens (Fig. 5b). Both medium Mn steel and TWIP steel were electrochemically H-charged for 48 h, and underwent TDA at a heating rate of 100°C/h. Both reference steels showed the higher H desorption rate peaks most likely due to a longer charging time of 48 h. The dual-phase medium Mn steel exhibited a narrow peak ranging from room temperature to 100°C and a low peak temperature (~65°C). The TWIP steel revealed a peak temperature range similar to the HRAH and CRAH specimens and a high peak temperature (~110°C). In an aspect of peak temperature, the peak temperature of HRAH and CRAH specimens (~80°C) is in between those of medium Mn steel without γR and full austenitic TWIP steel. This result indicates that the H desorption rate peaks of HRAH and CRAH specimens with ~50% γR were generated by H detrapped from both α and γR, and that the peak temperature increases with increasing volume fraction of γR most likely due to both a slow diffusion rate and a high solubility of H in γR [35,36].

Therefore, the separation of H desorption rate peaks of HRAH and CRAH specimens was carried out. As shown in Fig. 5c, the H desorption rate peaks were separated into two different peaks. The first peak appeared at the temperatures ranging from room temperature to ~120°C and its peak temperature was ~65°C, corresponding to the peak temperature of α. The second peak was ranged from room temperature to ~200°C and its peak temperature was ~110°C, matching well with the peak temperature of γR. The second peak is larger than the first peak; this means that γR has more diffusible H than α due to its high solubility of H. Namely, γR traps H more strongly compared to α in medium Mn TRIP steels [19]. An average concentration of diffusible H detrapped from γR grains was ~0.9 mass ppm and that of diffusible H detrapped from α grains was ~0.3 mass ppm.

The H-uncharged and charged HRA and CRA specimens underwent the SSRT to examine the HE behavior; their engineering stress-strain curves are shown in Fig. 6a. Regarding the H-uncharged specimens, the HRA specimen exhibited continuous yielding, and had a yield strength (YS) of 637 MPa, an ultimate tensile strength (UTS) of 1227 MPa, a uniform elongation (UEL) of 22.1% and a total elongation (TEL) of 24.3%. The CRA specimen showed discontinuous yielding with a Lüders strain of 3.3%, and had an upper YS of 899 MPa, a lower YS of 864 MPa, a UTS of 1397 MPa, a UEL of 19.4% and a TEL of 21.8%. Present authors have reported that the difference in yielding behavior between the HRA and CRA specimens was caused by the difference in strength of γR, and that step-like flow curves were due to the TRIP phenomenon; the γR grains with low phase stability first underwent α′ martensitic transformation, and then the γR grains with high phase stability were transformed later [1].

Meanwhile, the H-charged specimens revealed premature fracture without necking. Whereas the YS and the initial strain hardening rate of the H-charged specimens were almost identical to those of the H-uncharged specimens, the TEL dramatically decreased to 3.1% for the HRAH specimen and to 5.6% for the CRAH specimen. The reduction in TEL corresponds to an elongation loss of ~0.87 for the HRAH specimen and ~0.74 for the CRAH specimen, which was calculated by the following equation.
Elongation loss = 1 - (TEL of the H-charged specimen/TEL of the H-uncharged specimen) \[ (2) \]

To examine the phase stability of $\gamma_R$ in both HRA and CRA specimens, the variation of the volume fraction of $\gamma_R$ with engineering tensile strain was measured through XRD tests (Fig. 6b). The volume fraction of $\gamma_R$ decreased continuously with increasing tensile strain to reach almost zero at strains of over ~20% in both specimens. This indicates that both HRA and CRA specimens have a similar mechanical stability of $\gamma_R$ because the volume fraction (Fig. 2b) and the Mn and C concentrations (Fig. 4c) of $\gamma_R$ were almost identical in both specimens except for the morphology of $\gamma_R$ grains. Therefore, it was realized that mechanical stability of both specimens is more strongly influenced by chemical composition than the size and morphology of $\gamma_R$ grains.

To clarify the cause of premature fracture of the HRAH specimen, the fractured surfaces of both H-uncharged and charged specimens were observed using the SEM (Fig. 7). Whereas the HRA specimen revealed ductile fracture featured by fine dimples (Fig. 7a), the HRAH specimen exhibited both flat fractured surfaces (Fig. 7b and c) and cracks propagating along the boundaries (Fig. 7b). The size of the traces of detached grains (~37 μm) was similar to that of prior $\gamma$ grains (~35 μm, Fig. 1a). Accordingly, it is thought that intergranular fracture occurred along the boundaries of prior $\gamma$ grains which partially remained even after intercritical annealing [1,11]. The detached boundaries revealed rugged facets, as shown in Fig. 7c.

To investigate the fracture mode more in detail, the fractured surface of the HRAH specimen was observed at a low magnification from a normal direction using the SEM (Fig. 8a). Many cracks were observed at both edges of the tensile specimen. A location slightly away from a crack (region I) and a part of a large crack (region II) were observed using the SEM-EBSD. It was realized that cracks were initiated at the junctions of prior $\gamma$ grain boundaries (‘1’ in Fig. 8b and c taken at the region I) and propagated along the grain.

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Fig. 5. (a) H desorption rate curves of H-charged HRA (HRA_H) and CRA (CRA_T) specimens. (b) H desorption rate curves of present HRA_H and CRA_T steels, Fe-5.8Mn-0.1C-3.1Al-0.5Si (wt.%) steel with ferrite and $\alpha'$ martensite [19] and Fe-18Mn-0.6C (wt.%) austenitic steel [34]. The two reference steels were H-charged for 48 h. (c) Peak separation of H desorption rate curves of both HRA_H and CRA_T specimens.

Fig. 6. (a) Engineering stress-strain curves of H-uncharged HRA and CRA specimens and H-charged HRA_H and CRA_T specimens. (b) Changes in the volume fraction of retained austenite ($\gamma_R$) as a function of engineering strain in the four specimens.
boundaries (‘2’ in Fig. 8b and c taken at the region I and Fig. 8d taken at the region II). This result confirms that the HRAH specimen was broken by intergranular fracture occurring along the boundaries of prior γ grains.

Meanwhile, to observe the surface morphology of detached grain boundaries, a vicinity of a crack (a white box in Fig. 8d) was enlarged. As shown in Fig. 8e, whereas the upper part showed a rugged surface, the lower part exhibited a relatively flat surface. At the rugged surface, several micro-cracks intruded into the γL grains, which are located near the boundaries of prior γ grains. This
phenomenon can be explained as follows:

The $\gamma_L$ grains near a main intergranular crack were stress-concentrated to undergo strain-induced $\alpha'$ martensitic transformation (white arrows in Fig. 8e). This was also confirmed by the fact that the volume fraction of $\gamma_L$ (~0.12) near the main crack is lower than the initial volume fraction of $\gamma_L$ (~0.47). When strain-induced martensitic transformation occurred, H inside the $\gamma_L$ was inherited into $\alpha'$ martensite; H-enriched martensite was so brittle that it provided a nucleation site for micro-cracks. However, when the $\gamma_L$ grains were not located near the main intergranular crack, the main crack was propagated only along the H-enriched boundaries of prior $\gamma$ grains. Therefore, no micro-cracks formed at the strain-induced martensite, resulting in the flat surface. This analytical result ensures that the flat surface as well as the rugged surface observed in Fig. 7b and c was not caused by the transgranular fracture, but by the intergranular fracture.

This intergranular fracture has been usually explained by the HEDE mechanism that dissolved H reduces the cohesive bonding energy between lattice atoms [24,25] or the internal pressure mechanism operating by the formation of a H$_2$ gas at the crystal defects [22,23]. Because the latter mechanism is observed in severely H-charged steels with a high current density of ~500 A m$^{-2}$ [23,37], where blisters form on the specimen surface, it is thought that the present HRA$_H$ specimen revealed intergranular fracture most likely by the HEDE mechanism. Du et al. [38] performed the density-functional theory (DFT) calculation to prove that H weakens the bonding of Fe atoms at grain boundaries to lower a critical strain required for intergranular fracture.

To investigate the reason for the premature fracture of the CRA$_H$ specimen, the fractured surfaces of H-uncharged (CRA) and charged (CRA$_H$) specimens were observed using the SEM. Both CRA (Fig. 9a) and CRA$_H$ (Fig. 9b) specimens exhibited fine dimples. Regardless of the specimen type, an average size of dimples was ~500 nm, which corresponds to the size of $\gamma_G$ and $\alpha_G$ grains (~450 nm, Fig. 3b). When the fractured surfaces of both specimens were observed again at a high magnification, it was realized that whereas the CRA specimen showed only empty dimples, a typical feature of ductile fracture (Fig. 9c), the CRA$_H$ specimen exhibited not only empty dimples (white arrows in Fig. 9d) but also dimples filled with grains (yellow arrows in Fig. 9d and e). The size of the traces of detached grains (~480 nm, Fig. 9e) was similar to those of $\gamma_G$ and $\alpha_G$ grains (~450 nm, Fig. 3b); this means that intergranular fracture occurred along the boundaries of $\gamma_G$ and $\alpha_G$ grains.

Accordingly, to investigate the fracture mechanism in the CRA$_H$ specimen more in detail, the fractured CRA$_H$ specimen was observed from a normal direction using the SEM-EBSD. When a
vicinity of the fractured edge (a white box in Fig. 10a) was zoomed in, many cracks with various sizes were observed (Fig. 10b). The region in a white box of Fig. 10b was observed using the SEM-EBSD (Fig. 10c). Cracks propagated along the high angle boundaries of grains with different crystallographic orientations; this indicates that intergranular cracking occurred in the CRAH specimen.

To examine a mechanism of intergranular cracking, some cracks in Fig. 10b were observed at a higher magnification (Fig. 11). SEM micrographs (Fig. 11a) and EBSD IQ-phase maps (Fig. 11b) provided the following information on the formation and propagation of cracks.

**Fig. 10.** (a) SEM micrograph taken at the normal direction of the fracture CRAH tensile specimen. (b) Highly magnified SEM micrograph taken at a white box in (a). (c) EBSD IPF map taken at a white box in (b).

**Fig. 11.** (a) SEM micrographs, (b) EBSD IQ-phase maps and (c) EBSD KAM maps taken near cracks in Fig. 10b. In SEM micrographs, α,G and αʹ,S are globular-shaped ferrite and strain-induced αʹ martensite, respectively. In EBSD IQ-phase map, austenite is green and ferrite or strain-induced αʹ martensite is red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
intergranular cracks. The cracks formed and grew along the interphase boundaries between \( \gamma_C \) and \( \alpha_C \) grains or the boundaries between \( \gamma_C \) grains because \( \gamma_C \) grains trapped H more strongly than \( \alpha_C \) grains (Fig. 5c). The \( \alpha' \) grains in Fig. 11a and b were transformed from the \( \gamma_C \) grains, which were stress-concentrated near the cracks.

From the above results, it was realized that the dimples filled with grains at the fractured surface of the CRAH specimen (Fig. 9d and e) resulted from intergranular cracking occurring along the boundaries of \( \gamma_C \) grains by the HEDE mechanism [24,25]. Meanwhile, the formation of empty dimples, which are not filled with grains, is considered to be related to the cracking inside the \( \alpha_C \) grains. This speculation came from the fact that the intergranular cracks of the CRAH specimen intruded into the \( \alpha_C \) grains (white arrows in Fig. 11a and b) unlike the HRAH specimen. To confirm the stress concentration at the \( \alpha_C \) grains at the tips of cracks, the kernel average misorientation (KAM) values were measured using the SEM-EBSD (Fig. 11c). The KAM analysis was conducted using an average misorientation angle around a measurement point with respect to a defined set of the nearest neighbor points. As expected, the \( \alpha_C \) grains at the tips of cracks exhibited the high KAM values (white arrows in Fig. 11c). Accordingly, it was realized that the intergranular cracks intruded into the \( \alpha_C \) grains and that a high density of dislocations formed near the intruded cracks because the KAM value is proportional to the microstrain caused by crystal defects, such as dislocations [39]. The internal cracks of the \( \alpha_C \) grains are considered to induce the empty dimples. Meanwhile, the reason why the \( \alpha_C \) grains in the CRAH specimen had the internal cracks unlike the \( \alpha_C \) grains in the HRAH specimen is thought to be the difference in the mobility of dislocations between \( \alpha_C \) grains and \( \gamma_C \) grains. Namely, the \( \alpha_C \) grains with a low initial density of dislocations are apt to undergo local plasticity by the high mobility of dislocations enhanced by H [26–28], resulting in crack propagation into the interior of the \( \alpha_C \) grains. This means that the HE of \( \alpha_C \) grains occurred by the HELP mechanism. However, the \( \alpha_L \) grains are difficult to experience local plasticity because the mobility of dislocations is hardly accelerated by H. The difficulty in increase of dislocation mobility by H is most likely because it is difficult to reduce the interactions between dislocations due to a high initial density of dislocations, although H reduces the stress field of a dislocation. The high initial density of dislocations in the \( \alpha_L \) grains was caused by inactive recrystallization during annealing [1]. This is the reason why the CRAH specimen did not exhibit the small empty dimples formed inside the \( \alpha_L \) grains by the HELP mechanism.

To clarify a difference of initial dislocation density between \( \alpha_C \) grains in the HRA specimen and \( \alpha_C \) grains in the CRA specimen, the KAM values of both \( \alpha_L \) grains and \( \alpha_C \) grains were measured using the EBSD IQ-phase maps (Fig. 3). The KAM analysis was conducted using the same method employed for Fig. 11c. The average KAM value of \( \alpha_L \) grains in the HRA specimen was \(-0.51\)° (Fig. 12a) and that of \( \alpha_C \) grains in the CRA specimen was \(-0.38\)° (Fig. 12b). This result indicates that an initial density of dislocations in \( \alpha_C \) grains of the HRA specimen was higher than that in \( \alpha_C \) grains of the CRA specimen.

In summary, the HRAH specimen was fractured only by intergranular cracking occurring along the prior \( \gamma \) grains according to the HEDE mechanism. The CRAH specimen was failed by intergranular cracking occurring along the boundaries of \( \gamma_C \) grains according to the HEDE mechanism and by intragranular cracking occurring inside the \( \gamma_C \) grains according to the HELP mechanism. The difference in propagation path of intergranular cracks was caused by the difference in microstructural morphology between the two specimens. Whether intragranular cracking occurs or not was determined by the difference in initial dislocation density between \( \alpha_C \) grains and \( \alpha_L \) grains. This difference in crack propagation path between the HRAH specimen and the CRAH specimen induced the difference in velocity of crack propagation, resulting in different elongation losses (Fig. 6a).

4. Conclusions

To investigate the HE mechanism in annealed medium Mn steel, the hot-rolled and annealed (HRA) specimen and the cold-rolled and annealed (CRA) specimen were used in the present study. Both specimens had a dual-phase microstructure of \( \gamma_R \) and \( \alpha \) with different morphologies, but similar volume fraction and chemical composition of each phase: a lath-shaped morphology for the HRA specimen and a globular-shaped morphology for the CRA specimen. By comparing tensile properties, fractographs and H desorption rate curves of H-uncharged and charged HRA and CRA specimens, the following new results were obtained:

(1) The H-charged HRA (HRAH) and CRA (CRAH) specimens exhibited a similar H concentration of \(-1.2\) mass ppm; the concentration of diffusible H detrapped from \( \gamma_R \) grains was \(-0.9\) mass ppm and that of diffusible H detrapped from \( \alpha \) grains was \(-0.3\) mass ppm. This result indicates that the morphologies of \( \gamma_R \) and \( \alpha \) did not significantly influence the H permeation and confirmed that H is more soluble in \( \gamma_R \) than in \( \alpha \).

(2) Whereas the HRA specimen was ductile-fractured to leave many dimples at the fractured surface, the HRAH specimen was brittle-fractured by intergranular cracking occurring along the boundaries of prior \( \gamma \) grains, which partially remained even after intercritical annealing, according to the HEDE mechanism. The fractured surface revealed both flat facets and rugged facets. When the \( \gamma_R \) grains were absent near the boundaries of prior \( \gamma \) grains, flat facets were observed. When the \( \gamma_R \) grains were present, cracks intruded into the \( \gamma_R \) grains, which had undergone the strain-induced \( \alpha' \) martensitic transformation, resulting in rugged facets.

(3) At first sight, both the CRA and CRAH specimens seemed to be ductile-fractured because of a dimple structure. However, in reality whereas the CRA specimen was ductile-fractured to leave only empty dimples, the CRAH specimen was fractured to leave both dimples filled with grains and empty dimples. The dimples filled with grains were generated by intergranular cracking occurring along the boundaries of \( \gamma_C \) grains according to the HEDE mechanism. The empty
dimples were made by intragranular cracking occurring inside the γe grains according to the HELP mechanism.

(4) The CRAH specimen exhibited a smaller elongation loss (−0.74) than the HRAH specimen (−0.87). This result was caused by the difference in crack path between the two specimens. Whereas cracks were propagated primarily along the boundaries of a few tens of micron-sized γ grains in the HRAH specimen, cracks were propagated by frequently changing their direction along the boundaries of nano-sized γe grains or into the α grains in the CRAH specimen.

References
