

**Effect of Grain Size on the
Hydrogen Embrittlement Behaviors in
High-manganese Austenitic Steels**

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Effect of Grain Size on the Hydrogen Embrittlement Behaviors in High-manganese Austenitic Steels



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Chapter 1 Background and purpose

1.1 Hydrogen embrittlement

It has been over 150 years since the negative effect of hydrogen on mechanical properties, known as hydrogen embrittlement, was reported by several researchers [1-3]. Hydrogen embrittlement is a phenomenon that degradation of mechanical properties, such as tensile strength, uniform elongation, fatigue life, fracture toughness, happens due to the presence of hydrogen in metals.

Hydrogen is inevitably absorbed into metals during fabrication process and service life. Except for the hydrogen existing in the matrix, some amount of absorbed hydrogen in metals is usually trapped at various lattice defects. **Figure 1.1** is a schematic illustration of various hydrogen trapping sites in metals. It has been reported that grain boundaries [4], dislocations [5] and coherent carbide interfaces [6] are the typical trapping sites for hydrogen whose activation energy for detrapping of hydrogen is low [7]. When hydrogen is trapped at these lattice defects, hydrogen is reversible, that is, hydrogen is easily detrapped and mobile at room temperature. The hydrogen trapped at these defects is called diffusible hydrogen. On the other hand, inclusions [8], voids [9] and incoherent carbide interfaces [6] have high activation energy for detrapping of hydrogen. They do not release hydrogen at room temperature

at all. The hydrogen trapped at these defects is called non-diffusible hydrogen. It is known that diffusible hydrogen plays an important role on hydrogen embrittlement during plastic deformation.

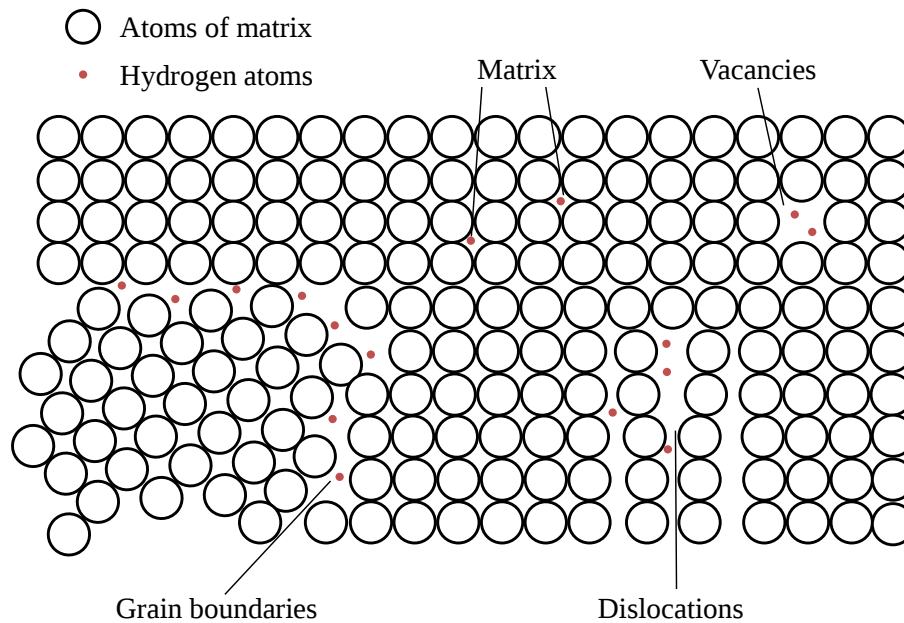


Figure 1.1 Schematic illustration of various defects that act as hydrogen trapping sites in metals.

1.1.1 Hydrogen embrittlement mechanisms

A great deal of research has been carried out to explain the mechanisms of hydrogen embrittlement in metals from different viewpoints. Several models have been proposed for hydrogen embrittlement: hydride-induced embrittlement [10-12], internal pressure mechanism [13, 14], hydrogen-enhanced decohesion (HEDE) [15, 16],

hydrogen-enhanced localized plasticity (HELP) [17, 18], and hydrogen-enhanced vacancy stabilization mechanism [19-21].

The hydride-induced embrittlement model suggests that hydrides nucleate in the stress-field near a crack and small hydrides coalesce to each other to form larger hydrides. Those hydrides are often brittle phase and induce the cleavage fracture. The alloying elements which tend to form hydrides and show hydrogen embrittlement are Ti, Zr, Nb, and V.

Internal pressure formation mechanism was proposed to explain embrittlement of steels. Hydrogen molecular is formed by dissolved hydrogen atoms in steels. As the hydrogen concentration in the matrix is reduced by molecular hydrogen precipitation, more hydrogen will diffuse into these regions, creating more molecular hydrogen and increasing the hydrogen pressure. The internal pressure formed by hydrogen molecular results in the creation of micro-cracks in the steels [22] and lowers the fracture stress.

Hydrogen-enhanced decohesion mechanism was first suggested by Troiano [23]. In this mechanism, hydrogen accumulates within a certain place of lattice and reduces the atomic bonding force of the metal lattice and promotes decohesion. However, direct experimental measurements and observation are difficult for proving this

mechanism.

Birnbaum et al. proposed that the presence of hydrogen enhances the dislocation mobility, which results in localized plastic deformation, so called hydrogen-enhanced localized plasticity [24, 25]. Robertson et al. directly observed hydrogen-enhanced localized plasticity using in-situ high voltage TEM deformation experiments [26]. According to their model, dislocation mobility is enhanced due to hydrogen accumulation at dislocation cores, resulting in reduced elastic energies of interaction between moving dislocations and a variety of obstacles [24]. The stress required for dislocation motion is decreased and plasticity is enhanced by the existence of hydrogen, resulting in the ductile fracture.

Hydrogen-enhanced strain-induced vacancy model have been proposed by Nagumo [27]. They insist that the primary function of hydrogen in degradation for mechanical properties is to enhance the strain-induced creation and agglomeration of vacancies, thus promoting the fracture process [28].

Although several models have been proposed for hydrogen embrittlement as mentioned above, the model that can consistently accounts for hydrogen embrittlement behaviors occurred in various materials under various conditions has not yet been established.

1.1.2 Hydrogen embrittlement behaviors of martensitic steels

It is well known that sensitivity to hydrogen embrittlement is enhanced with an increase in strength. Among typical high strength steels, martensitic steels are the major materials of hydrogen embrittlement investigation.

In martensitic steels, the degradation of mechanical property by hydrogen is significant. **Figure 1.2** shows nominal stress-strain curves of an AISI 4135 martensitic steel including various hydrogen contents ranging from 0 to 1.3 wt ppm [29]. While the specimen without hydrogen showed obvious yielding and necking before fracture, the specimen containing hydrogen exhibited limited plasticity and fractured at very small strain before obvious yielding.

Fracture mode of martensitic steels also changes from ductile to brittle after hydrogen addition. The typical hydrogen embrittlement fracture modes in martensitic steels are shown in **Figure 1.3**. **Figure 1.3 (a)** shows a quasi-cleavage fracture observed in a 2Mn-0.4C martensitic steel after hydrogen charging [30]. **Figure 1.3 (b)** shows an intergranular fracture in a 1.4Mn-0.3C martensitic steel after hydrogen charging [31].

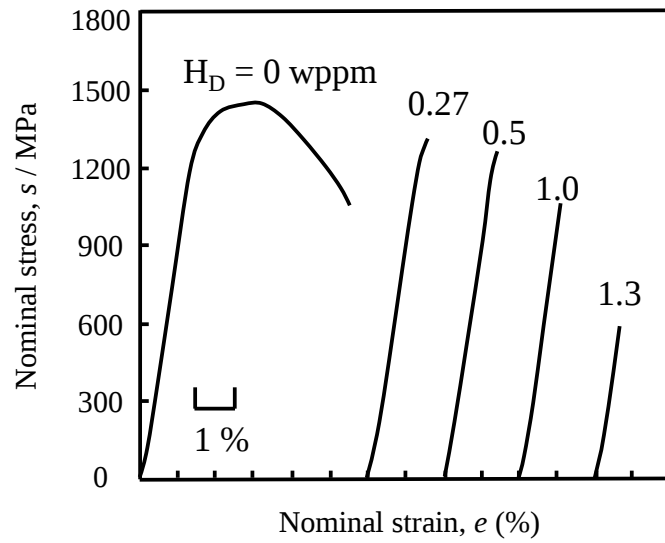


Figure 1.2 Nominal stress-strain curves of an AISI 4135 martensitic steel with different hydrogen contents obtained from slow strain rate tensile tests at room temperature [29].

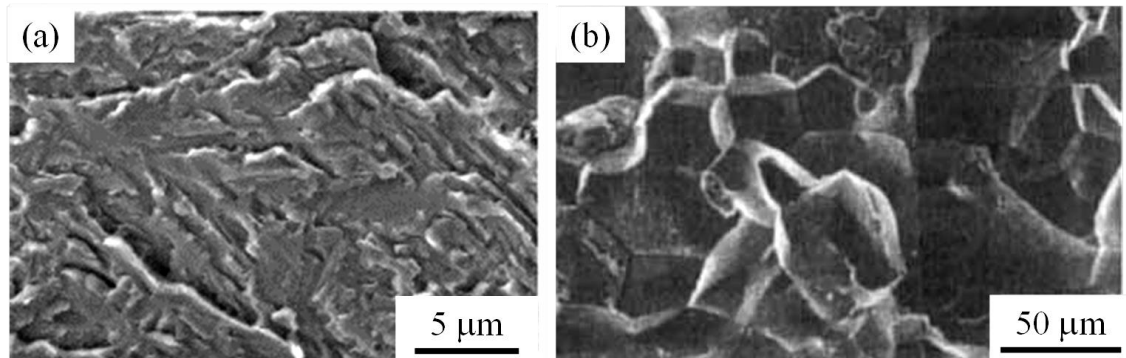


Figure 1.3 Typical hydrogen embrittlement fracture modes observed in high strength martensitic steels after hydrogen charging: (a) quasi-cleavage fracture in a 2Mn-0.4C martensitic steel [30], and (b) intergranular fracture in a 1.4Mn-0.3C martensitic steel [31].

The previous studies on hydrogen embrittlement of martensitic steels covered a large area including environmental factors, deformation conditions and microstructural parameters: hydrogen content, hydrogen trapping behavior, temperature, pre-staining, microstructure and crystallographic features of hydrogen-related cracks and so on. In

an AISI 4135 martensitic steel the fracture mode changed from ductile to brittle intergranular fracture after the introduction of a small amount of diffusible hydrogen [29]. Takai et al. [32] studied the hydrogen trapping sites in martensitic steel and revealed that hydrogen tends to accumulate at grain boundaries, segregation band and inclusions. Recently, Shibata et al. [33] studied the characteristics of hydrogen-related crack propagation in Fe-0.1C from microstructural and crystallographic points of view. Their results indicated that hydrogen-related fracture was due to the formation of micro-cracks around prior austenite grain boundaries and the subsequent crack propagation along block boundaries or lath boundaries. In addition, the technique of focused ion beam machining and transmission electron microscopy observation revealed that the intense slip bands formed beneath the hydrogen-related fracture surfaces [34]. According to the previous studies mentioned above, a considerable progress has been achieved in the studies of hydrogen embrittlement on martensitic steels.

1.1.3 Hydrogen embrittlement behaviors of austenitic steels

It is known that austenitic steels have high resistance to hydrogen embrittlement because of high solubility and low diffusivity of hydrogen in austenite phase with

Face-Centered Cubic (FCC) crystal structure. However, it has been reported that several austenitic stainless steels also show hydrogen embrittlement.

Figure 1.4 shows nominal stress-strain curves of an 18Cr-19Mn-0.8N (wt. %) austenitic steel with and without hydrogen [35]. As shown in **Figure 1.4**, the elongation and ultimate tensile strength decreased significantly in the austenitic steel tested in hydrogen atmosphere. However, the austenitic steel tested in a hydrogen gas atmosphere still exhibited approximately 12 % of plastic deformation. The fracture surface of the 18Cr-19Mn-0.8N (wt. %) austenitic steel tested in a hydrogen gas atmosphere showed brittle mode of intergranular fracture, as shown in **Figure 1.5**. Secondary cracks were also observed along grain boundaries. In addition, some very fine dimples (fractography of ductile fracture) covered the fracture surfaces, which indicated some extent of plastic deformation occurred.

Although degradation of mechanical properties and brittle fracture were observed both in martensitic steels and austenitic steels, apparent differences were also seen when comparing the hydrogen embrittlement behaviors between austenitic steels and martensitic steels. That is, the degree of degradation of mechanical properties was smaller than martensitic steels and the fractography was a mixture of brittle fracture and ductile fracture in austenitic steels.

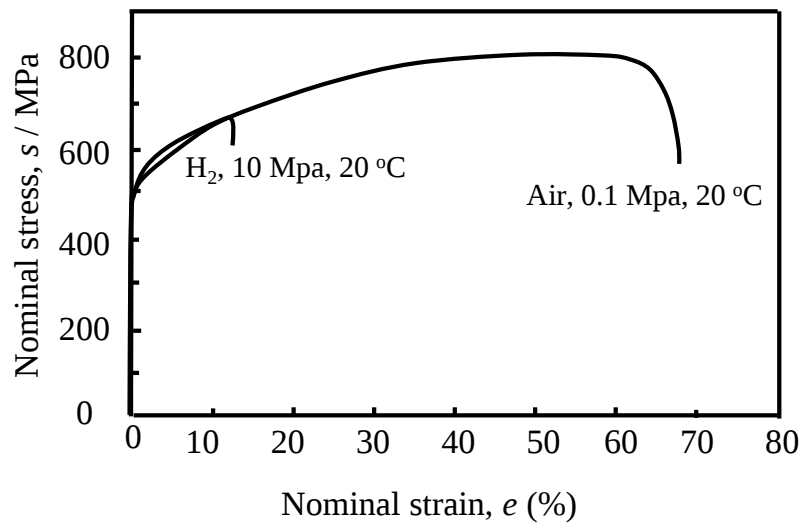


Figure 1.4 Nominal stress-strain curves of an 18Cr-19Mn-0.8N austenitic steel tested in hydrogen atmosphere and air [35].

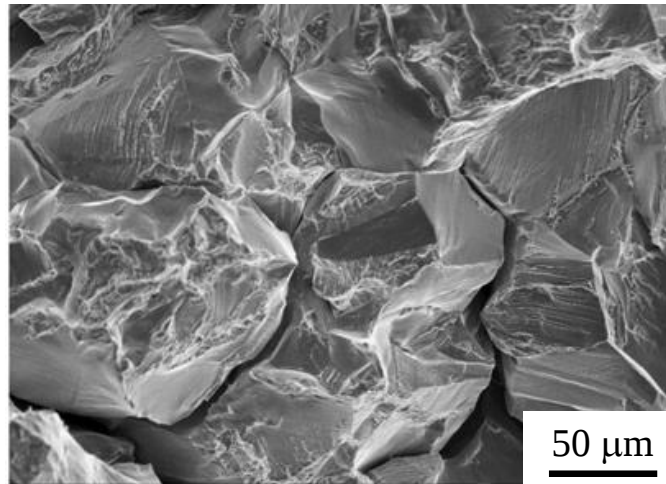


Figure 1.5 Fracture surface of an 18Cr-19Mn-0.8N austenitic steel tested in hydrogen atmosphere [35].

1.2 High-manganese austenitic steels

High-manganese austenitic steel is a new class of austenitic steel with relatively high strength and large ductility caused by the occurrence of deformation twinning during plastic deformation. These high-manganese austenitic steels are also known as twinning-induced plasticity (TWIP) steels [36].

1.2.1 Deformation mechanism of high-manganese austenitic steel

Slip and twinning are the most common and prominent deformation mechanisms in polycrystalline metals. Deformation twinning generally occurs in metals with Body-Centered Cubic (BCC) and Hexagonal Close-Packed (HCP) crystal structures under the conditions where slip process is restricted at low temperatures or at high strain rates. For metals having FCC structures, deformation twinning is observed when their stacking fault energy is low. Some high-manganese austenitic steels exhibit a large number of deformation twins even at ambient temperature.

Strength and ductility are two vital parameters for structural materials. However, the improvement of strength generally results in the reduction of ductility, which is known as a trade-off relationship between strength and ductility. Deformation

twinning brings about an outstanding balance of these two parameters. In high-manganese austenitic steels, a number of deformation twins form in grains with increasing stress. The deformation twins subdivide the grains and therefore increase the barriers against dislocation slips, resulting in the reduction of the mean free path of dislocations in grains. Such a phenomenon is known as dynamic Hall-Petch effect, and schematically illustrated in **Figure 1.6**. As a result, the deformed area is greatly hardened and the strain hardening rate increases, so that plastic instability is suppressed and results in large uniform elongation.

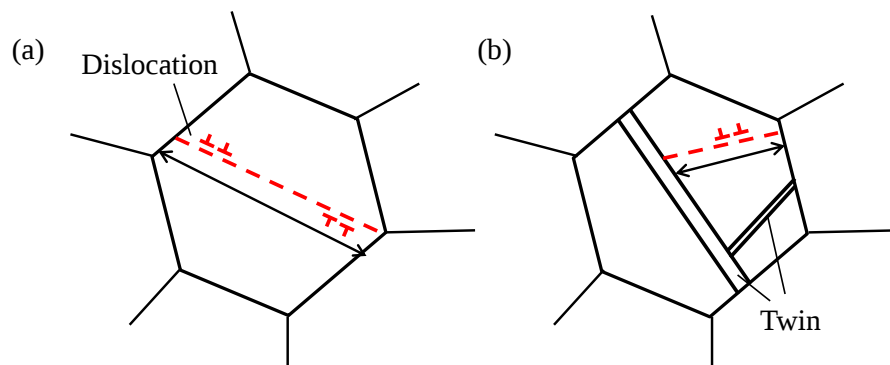


Figure 1.6 Schematic illustration of dynamic Hall-Petch effect. Red dashed lines indicate the mean free path of dislocations in a grain: (a) In case that only dislocation movement occurs, and (b) in case that dislocation movement and deformation twinning both occur.

1.2.2 Stacking fault energy

Stacking fault energy is an important parameter controlling the deformation mechanism in high-manganese steels, including: deformation twinning, dislocation slips, and martensitic transformation from FCC γ phase to HCP ϵ phase. Formation of deformation twins in high-manganese austenitic steels during deformation is due to their relatively low stacking fault energy (SFE) of the austenite matrix.

SFE can be calculated on the basis of consideration that an intrinsic stacking fault is equivalent to a platelet ϵ -martensite with a thickness of only two atomic layers creating two new γ/ϵ interfaces [37]. The SFE is given by Hirth [38] as,

$$\text{SFE} = 2\rho \Delta G^{\gamma \rightarrow \epsilon} + 2\sigma^{\gamma/\epsilon} \quad (1.1)$$

where ρ is the surface density of atoms in $\{111\}\gamma$ plane, $\Delta G^{\gamma \rightarrow \epsilon}$ is the change in free energy corresponding to the $\gamma \rightarrow \epsilon$ transformation, and $\sigma^{\gamma/\epsilon}$ is the interfacial energy between γ and ϵ .

The SFE and deformation mode in austenitic steels are generally summarized as below: martensitic transformation ($\gamma \rightarrow \epsilon$) takes place in the austenite having a very lower SFE ($\gamma_{\text{fcc}} \leq 20 \text{ mJ / m}^2$). On the contrary, a higher SFE ($\gamma_{\text{fcc}} > 50 \text{ mJ / m}^2$) results in only dislocation movement. It has been believed that for the austenitic steels whose

SFE is ranging between 20-50 mJ / m², γ to ϵ phase transformation is suppressed and deformation twinning is enhanced accompanying with slip deformation, which results in a large work hardening and good ductility [39, 40].

Except chemical composition, the value of SFE of a material is also influenced by temperature as well as grain size. SFE shows an increasing trend with increasing the temperature or decreasing the grain size [41]. So, even in the same material, the SFE can differ by changing the grain size.

1.2.3 Typical high-manganese austenitic steels

Chemical composition of the alloy changes SFE [42], thereby affects the deformation mode. Frommeyer et al. [43] have conducted systematic works on the effect of manganese on the mechanical properties in high-manganese austenitic steels.

Figure 1.7 shows the true stress-strain curves of (15-25)Mn-3Al-3Si (mass %) austenitic steels at room temperature. The austenitic steels with 15 mass % of manganese exhibited a change in the curvature on the stress-strain curve at higher strains larger than 0.15. The increasing curvature, i.e., a significant increase in the work hardening rate, is due to the deformation-induced martensitic transformation.

This feature of the stress-strain curve is typical for transformation-induced plasticity (TRIP) steels. The austenitic steel with 25 mass % of manganese did not show any change in the curvature of the stress-strain curve even at high strains. A high density of deformation twins were observed in the tensile deformed high-manganese austenitic steel with 25 mass % of manganese. The result indicated that the chemical composition is an important factor to affect the SFE and deformation mechanism in high-manganese steels.

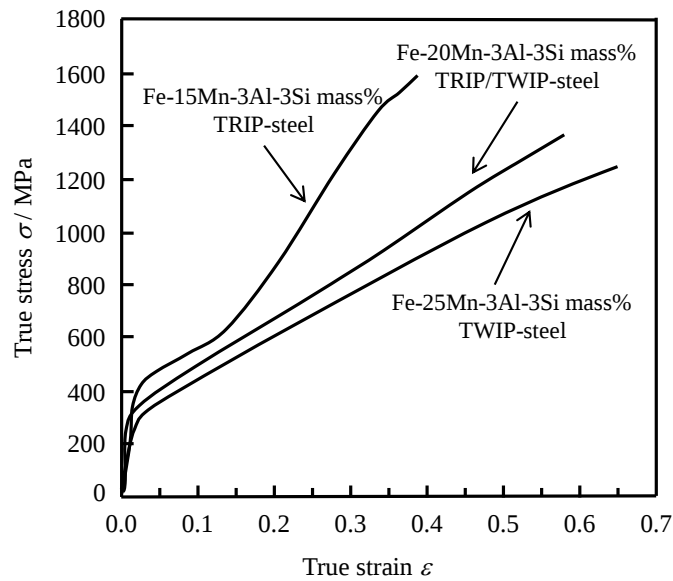


Figure 1.7 Comparison of true stress-strain curves of the high-manganese austenitic steels with different manganese contents [43].

The main chemical compositions of the high-manganese austenitic steels which exhibit deformation twinning (i.e., TWIP steel) are manganese (Mn), carbon (C), aluminum (Al), and silicon (Si). The effects of these main alloying elements in

high-manganese austenitic steels are summarized in **Table 1.1**. Carbon is an austenite stabilizing alloying element and it is needed to obtain high strength by solution strengthening [44]. Manganese is a main austenite stabilizing element [45]. Addition of manganese into austenitic steels increases ductility. Aluminum increases the SFE of austenite matrix and therefore strongly suppresses the $\gamma \rightarrow \epsilon$ martensitic transformation [44], while silicon decreases SFE and enhances the $\gamma \rightarrow \epsilon$ martensitic transformation [46]. Accordingly, deformation twinning can be obtained by only proper combination of the alloying elements.

Table 1.1 Summary of the effects and content of main alloying elements in high-manganese austenitic steels.

Element	Effect	Content (wt. %)
Mn	Stabilize the austenite, increase the plasticity [45]	15-30
C	Enhance strength [44], reduce the ductility	0.5-1.0
Al	Increase the SFE, suppress martensitic transformation [44]	<10
Si	Decrease the SFE, sustain martensitic transformation [46]	<3

Figure 1.8 [47] represents the relationship between strength and ductility of various kinds of steels used in automobile industries, including the high-manganese austenitic steels having deformation twinning effect (TWIP steels). In most of the

materials, the strength-ductility profiles indicate an inverse relationship. Among the materials shown in **Figure 1.8**, high-manganese austenitic steels possess better combination of high strength and large ductility than other class of steels. Till now, three kinds of typical high-manganese austenitic steels, Fe-Mn-C [48], Fe-Mn-Al-C [49], and Fe-Mn-Al-Si [50], have been developed. **Table 1.2** summarizes the tensile properties (yield strength, tensile strength and total elongation) of the typical high-manganese austenitic steels having deformation twinning effect.

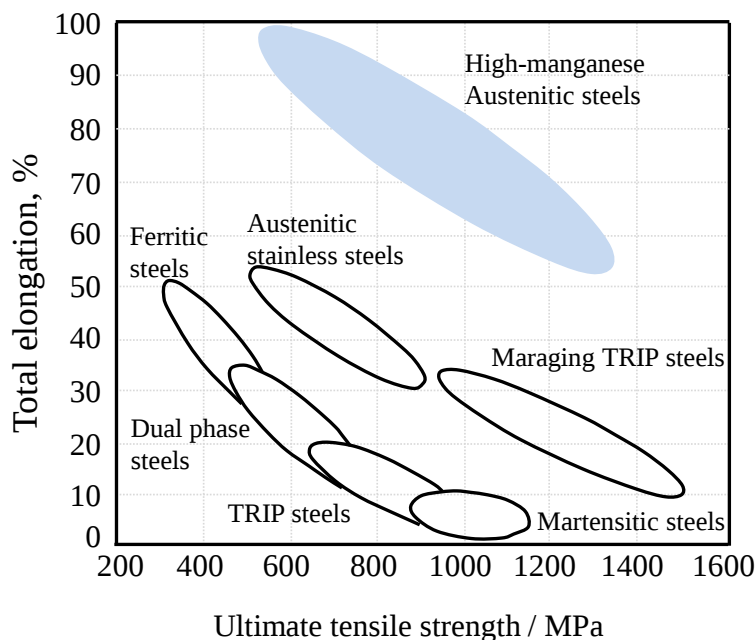


Figure 1.8 Relationship between tensile strength and total elongation of various structural steels [47].

Table 1.2 Summary of tensile properties of typical high-manganese austenitic steels.

Chemical composition (wt. %)	Yield strength σ_y / MPa	Ultimate tensile strength σ_{UTS} / MPa	Total elongation e (%)	Reference
Fe-18Mn-0.6C	440	1080	74	[48]
Fe-22Mn-0.6C	450	1160	55	[51]
Fe-18Mn-2Al-0.6C	210	700	70	[49]
Fe-30Mn-3Al-3Si	250	610	88	[50]

1.3 Grain refinement

Materials can be strengthened by precipitates, solid solution, grain refinement, and so on. For a single-phase alloy, grain refinement is the simplest way to strengthen the material without any change in the chemical composition.

Bulk nanostructured materials (or ultrafine-grained materials) of which grain size of the matrix phase is smaller than 1 μm have been attracting a great interest over two decades. Bulk nanostructured materials can be obtained by several ways. Severe plastic deformation (SPD) methods are well-investigated for fabricating ultrafine-grained metals by introducing a large amount of plastic strains into a bulk metal. Representative SPD processes are, for example, equal-channel angular pressing (ECAP) [52], high-pressure torsion (HPT) [53], and accumulative roll bonding (ARB) [54]. **Figure 1.9** schematically illustrates the process of each SPD method. ECAP introduces severe plastic deformations into the material by repeating a simple shear deformation through a channel die having an angle of typically 90° (sometimes from 90° to 120°). In the case of HPT process, sample is placed in a closed die and a large pressure and torsion strain are imposed to the sample. In the ARB process, two pieces of sheets with the same thickness are stacked and roll-bonded by 50 % reduction in thickness per rolling cycle. The rolled-bonded sheets are cut into two, stacked, and the

same procedures are repeated several times so that large plastic strains could be imposed to the materials.

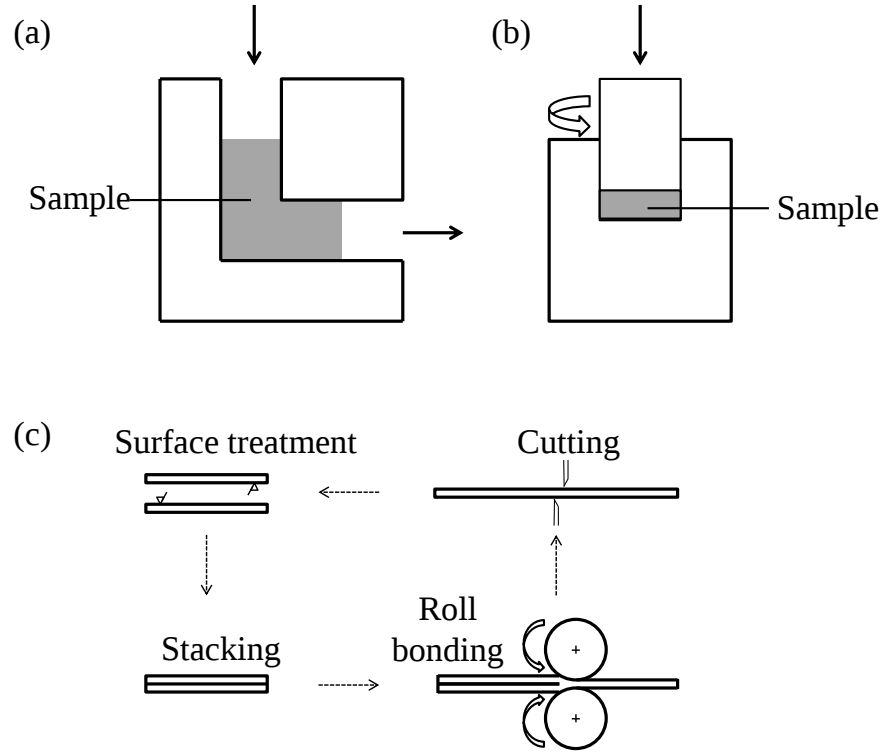


Figure 1.9 Schematic illustrations of major SPD processes: (a) equal-channel angular pressing (ECAP) [52], (b) high-pressure torsion (HPT) [53], and (c) accumulative roll bonding (ARB) [54].

The relationship between the grain size and the yield strength can be described by Hall-Petch relationship shown in the following equation:

$$\sigma_y = \sigma_0 + k_y \times d^{1/2} \quad (1.2)$$

where σ_y is the yield strength, σ_0 is the friction stress, k_y is a constant, and d is the mean

grain size. According to **Equation 1.2**, the strength increases with decreasing the mean grain size. However, it is well known that a trade-off relationship exists between strength and ductility, i.e., elongation generally decreases with increasing strength. Kamikawa [55] fabricated various grain sized IF steel by ARB process and subsequent annealing. **Figure 1.10** shows nominal stress-strain curves of the IF steel with various grain sizes ranging from 0.21 μm to 12 μm . Although the yield strength dramatically increased with decreasing the grain size, the uniform elongation significantly reduced to only a few percent. This phenomenon can be explained by the following formula, namely plastic instability condition;

$$\sigma \geq d\sigma / d\varepsilon \quad (1.3)$$

where σ is the true flow stress, ε is the true strain, and $d\sigma / d\varepsilon$ is the work-hardening rate. According to **Equation 1.3**, necking occurred when the work hardening rate becomes smaller than the flow stress. Kamikawa [55] found that the work-hardening rate after yielding decreases with decreasing the grain size in the IF steel with various grain sizes. As a result, necking occurred at very early stage of the tensile test in the ultrafine-grained (0.29 μm and 0.76 μm) materials. Accordingly, the way to balance high strength and large ductility is to enhance work-hardening rate.

Recently, a 31Mn-3Al-3Si steel with fully recrystallized microstructure and mean grain size smaller than 1 μm was fabricated [56]. Nominal stress-strain curves of the ultrafine-grained Fe-31Mn-3Al-3Si specimens and the coarser-grained specimens are shown in **Figure 1.11**. Compared with the coarse-grained specimens [40], the ultrafine-grained specimen with the grain size of 400 nm still possesses a good balance of strength and ductility. The outstanding mechanical properties would be attributed to the high work hardening rate by deformation twinning during tensile test.

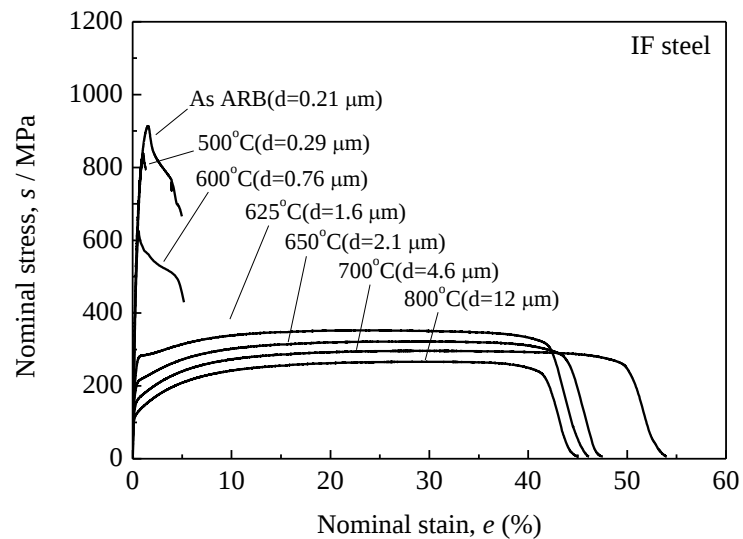


Figure 1.10 True stress-strain curves of the IF steel with various grain sizes produced by ARB and subsequent annealing [55].

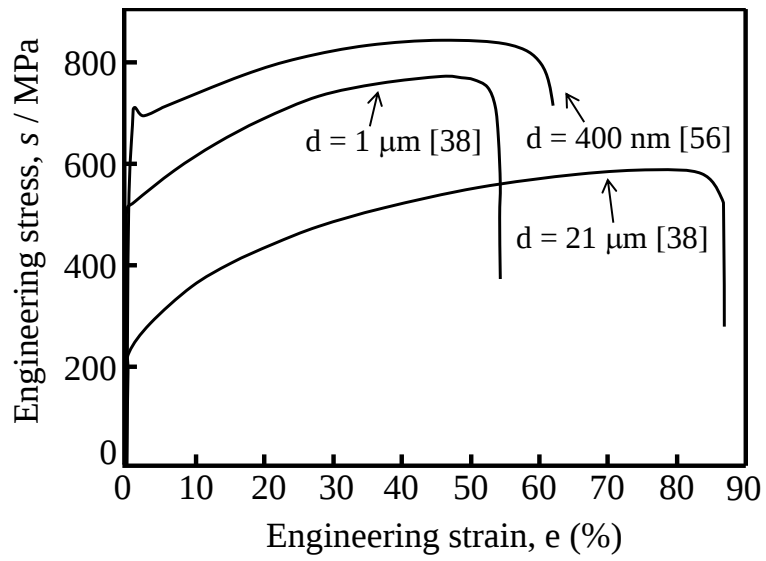


Figure 1.11 Engineering stress-strain curves of the 31Mn-3Al-3Si steels with various grain sizes fabricated by cold-rolling and subsequent annealing, with grain sizes of 400 nm [56], 1 μm [40] and 21 μm [40].

1.4 Objective of the present thesis

High-manganese austenitic steel has been attracting a great attention especially from the automobile industry due to their high strength and large ductility. Nowadays, it has been found that ultrafine-grained structures can be fabricated in high-manganese austenitic steels by conventional cold-rolling and subsequent annealing [56]. Compared with the high-manganese austenitic steels with conventional grain sizes, the ultrafine-grained high-manganese austenitic steels show much higher strength but do not lose ductility [40, 56]. However, hydrogen embrittlement susceptibility of steels is generally enhanced by increasing the strength. Accordingly, hydrogen embrittlement properties should be taken into consideration for applying the high-manganese austenitic steels having ultrafine grains to practical applications.

In recent years, several groups studied hydrogen embrittlement behaviors in high-manganese austenitic steels [48, 48, 56, 57]. **Table 1.3** summarizes the previous research about hydrogen embrittlement in high-manganese austenitic steels. Koyama and co-workers reported that intergranular fracture occurred and fracture stress decreased with increasing the hydrogen content in an 18Mn-0.6C steel [48]. They also revealed from microstructural observation that hydrogen-assisted cracking in an 18Mn-1.15C steel initiated and propagated along both grain boundaries and deformation

twins [57]. Furthermore, they reported that hydrogen-induced delayed fracture in an 22Mn-0.6C steel was suppressed by increasing the strain rate of the pre-deformation [49]. Park et al. [57] studied hydrogen embrittlement behaviors of Ti-bearing high-manganese austenitic steels and revealed that fracture mode changed from ductile to brittle with increasing the Ti content. As mentioned above, the hydrogen embrittlement behaviors of several high-manganese austenitic steels have been becoming clear.

Table 1.3 Summary of researches on hydrogen embrittlement in high-manganese austenitic steels.

Material	Issue	Reference
Fe-18Mn-0.6C	Effect of hydrogen content	[48]
Fe-18Mn-1.15C	Influence of deformation twins on hydrogen-assisted cracking	[57]
Fe-22Mn-0.6C	Effect of pre-strain at different strain rate	[51]
Fe-18Mn-0.6C-2Al-xTi	Effect of Ti precipitates on hydrogen embrittlement	[58]

So far, however, the effect of grain size below 1 μm on hydrogen embrittlement behaviors of high-manganese austenitic steels has not yet been well understood. Accordingly, the purposes of the present study are as follows:

1. To fabricate fully recrystallized Mn-Al-Si and Mn-C high-manganese austenitic steels with grain sizes ranging from coarse to ultrafine scales through conventional cold rolling and subsequent annealing.
2. To clarify the effect of grain size on hydrogen embrittlement behaviors of the various grain-sized high manganese austenitic steels. Especially, the changes in mechanical properties and the feature of fracture surfaces will be investigated in the different grain-sized specimens. Also the hydrogen contents, hydrogen distribution, and hydrogen concentration will be investigated in the different grain-sized specimens.
3. To reveal the effect of grain size on the initiation and propagation behaviors of hydrogen-related cracks from a microstructural viewpoint.

1.5 Outline of the dissertation

The present dissertation consists of six chapters.

In **Chapter 1**, the background and purpose of this dissertation are introduced.

In **Chapter 2**, cold-rolling and subsequent heat treatment are carried out to fabricate fully recrystallized single-phase austenite structures with various grain sizes ranging from micrometer scale to submicro-meter scale in bulk 31Mn-3Al-3Si and 22Mn-0.6C steels by the use of the processes without severe plastic deformation.

In **Chapter 3** and **Chapter 4**, the effect of grain size on hydrogen embrittlement behaviors in the two kinds of high-manganese austenitic steels are evaluated by an uniaxial slow strain rate tensile test at room temperature after hydrogen pre-charging. The hydrogen embrittlement behaviors are investigated from the aspects of the changes in hydrogen content, mechanical properties, and fracture surfaces in each grain-sized hydrogen-charged and uncharged specimen.

In **Chapter 5**, in order to figure out the different hydrogen embrittlement behaviors in the different grain-sized specimens, hydrogen-related crack initiation and propagations behaviors in the 31Mn-3Al-3Si and 22Mn-0.6C steels are investigated by microstructural characterization through interrupted tensile tests using double-notch

tensile test specimens.

In **Chapter 6**, conclusions and new findings in the present research are summarized.

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Chapter 2 Fabrication of various grain-sized high-manganese austenitic steels by conventional cold rolling and subsequent annealing

2.1 Introduction

Recently, several researches have fabricated ultrafine-grained structures in high manganese austenitic steels. Matoso et al. [1] fabricated an ultrafine-grained structure in a 24Mn-3Al-2Si-1Ni-0.06C steel by high pressure torsion, and revealed that micro hardness of the ultrafine-grained structure was 450 HV and much higher than that of the coarse-grained one (180 HV). Timokhina et al. [2] obtained mean grain sizes ranging from 0.3 μm to 0.6 μm by equal-channel angular pressing (ECAP) and subsequent annealing in a 0.61C-22.3Mn-0.19Si-0.14Ni-0.27Cr steel. Santos et al. [3] fabricated a recovered or partially recrystallized ultrafine-grained structure in a 24Mn-3Al-2Si-1Ni-0.06C steel by 42 % cold rolling and annealing at temperatures between 600 °C and 850 °C for 0.3 ks. The result indicated that the ultrafine-grained specimens showed good mechanical properties (**Figure 2.1(a)**, indicated by red line). In addition, a 25Mn-2.8Al-2.4Si-0.08C steel with an mean grain size of 0.06 μm was successfully produced by combination of asymmetric rolling plus symmetric rolling and subsequent annealing [4]. The nano-grained structure was partially recrystallized and

showed excellent mechanical properties of high strength and good ductility (**Figure 2.1(b)**, indicated by red line)).

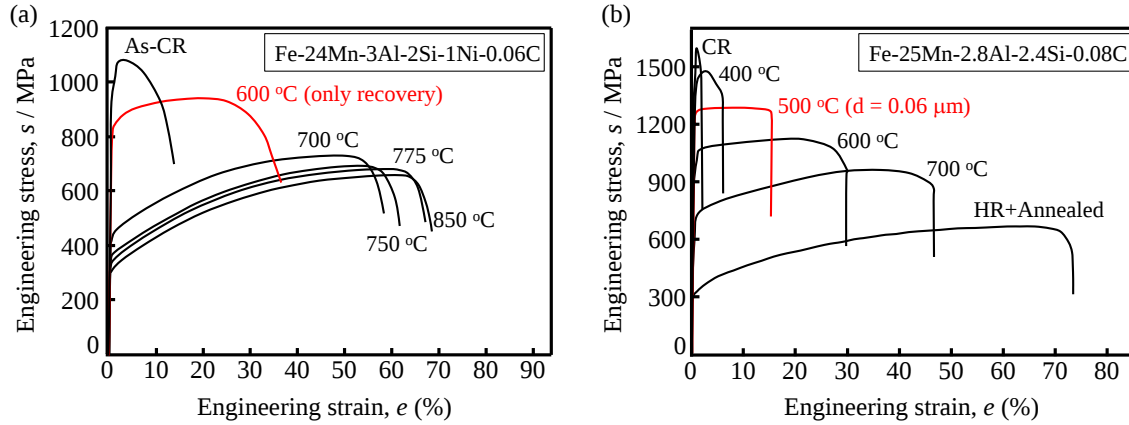


Figure 2.1 Nominal stress-strain curves of high-manganese steels fabricated by different rolling and annealing processes: (a) cold-rolled to 42 % reduction in thickness and isochronally annealed at temperatures between 600 °C and 800 °C [3], (b) asymmetric rolling and symmetric rolling with a total reduction of 98 % followed by subsequent annealing between 400 °C and 700 °C [4].

Saha et al. [5] reported that a fully recrystallized austenitic structure with a mean grain size of $0.4 \mu\text{m}$ was obtained in a 31Mn-3Al-3Si austenitic steel through 92 % cold rolling and subsequent heat treatment at 650 °C for 0.3 ks followed by water quenching. The ultrafine-grained 31Mn-3Al-3Si steel exhibited high yield strength, good strain hardening, and large tensile elongation. Their result suggested that bulk high-manganese austenitic steels with fully recrystallized ultrafine grains could be obtained by conventional cold rolling and subsequent heat treatment without severe plastic deformation.

In this chapter, two kinds of typical high-manganese austenitic steels with different chemical compositions were used to fabricate various grain sizes ranging from coarse grain scale to ultrafine grain scale by conventionally heavy cold rolling and subsequent annealing. The process for the 31Mn-3Al-3Si steel is based on the method proposed by Saha et al. [6].

2.2 Materials and experimental procedures

2.2.1 Fabrication processes of various grain-sized specimens

2.2.1.1 31Mn-3Al-3Si austenitic steel

A 31Mn-3Al-3Si (wt. %) austenitic steel was used in the present study. The chemical composition of the used alloy is given in **Table 2.1**. The as-received hot-rolled plate is called starting material hereafter.

Table 2.1 Chemical composition of the Mn-Al-Si austenitic steel studied (wt. %).

Mn	Si	Al	C	N	S	Fe
31	3.0	3.0	0.005	0.004	0.012	Bal.

The starting material with a thickness of 12 mm was cold-rolled to 1mm thickness with a total reduction of 92 % (the equivalent strain $\varepsilon = 2.87$) by multi-pass rolling. A two-high rolling mill with a roll diameter of 250 mm was used for cold rolling under a lubricated condition at room temperature. In order to fabricate specimens with various grain sizes, the 1 mm thick cold-rolled sheet was subsequently annealed at temperatures of 650 °C, 725 °C, 800 °C, or 900 °C for 0.3 ks in a salt bath followed by water quenching or annealed at 1000 °C for 1.8 ks in a quenching furnace under vacuum followed by water quenching. The fabrication processes of the specimens having

various grain sizes are schematically illustrated in **Figure 2.2**.

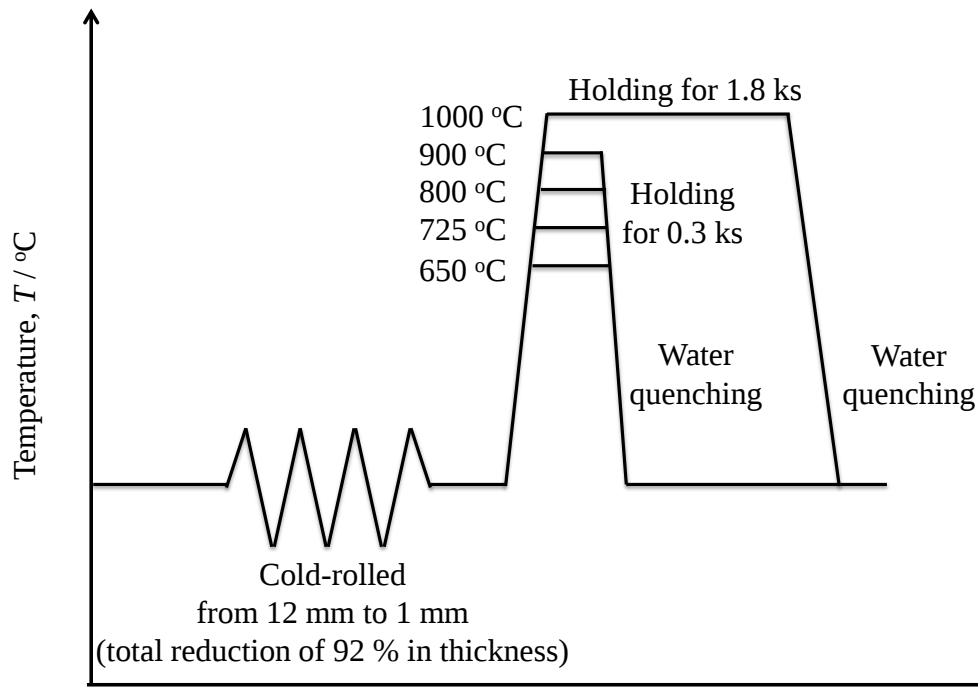


Figure 2.2 Schematic illustration of the thermomechanical processes for the 31Mn-3Al-3Si steel.

2.2.1.2 22Mn-0.06C austenitic steel

A 22Mn-0.6C (wt. %) austenitic steel was also used. The chemical composition of the steel is shown in **Table 2.2**. The as-received hot-forged plate 12 mm thick is called starting material hereafter.

Table 2.2 Chemical composition of the Mn-C austenitic steel studied (wt. %).

Mn	C	Si	P	Al	S	N	Fe
21.68	0.56	0.06	<0.004	<0.01	0.007	0.004	Bal.

The starting material with a thickness of 12 mm was cold-rolled to 1 mm thickness by four steps of the processes including multi-pass rolling (a total reduction of 92 %, the equivalent strain $\varepsilon = 2.87$) and annealing. A two-high rolling mill with a roll diameter of 250 mm was used for cold rolling under a lubricated condition at room temperature. **Figure 2.3** shows a schematic illustration of the four-step fabrication process. At first, the starting material was cold-rolled from thickness of 12 mm to 8 mm and annealed at 600 °C for 0.6 ks followed by water quenching. Then the 8 mm cold-rolled and annealed sheet was cold-rolled to 5 mm, annealed at 600 °C for 0.6 ks and water-quenched in the second step. The 5 mm thick sheet was again cold-rolled to 3 mm, annealed at 600 °C for 0.6 ks and water-quenched. In the last step, to control the grain size finally, the 3 mm thick sheet was cold-rolled to 1 mm, annealed at 550 °C and 850 °C, respectively, followed by water quenching. The reduction applied in each cold rolling step was 33.3 %, 37.5 %, 40 % and 66.7 %, respectively, and the total reduction in this process was 92 %.

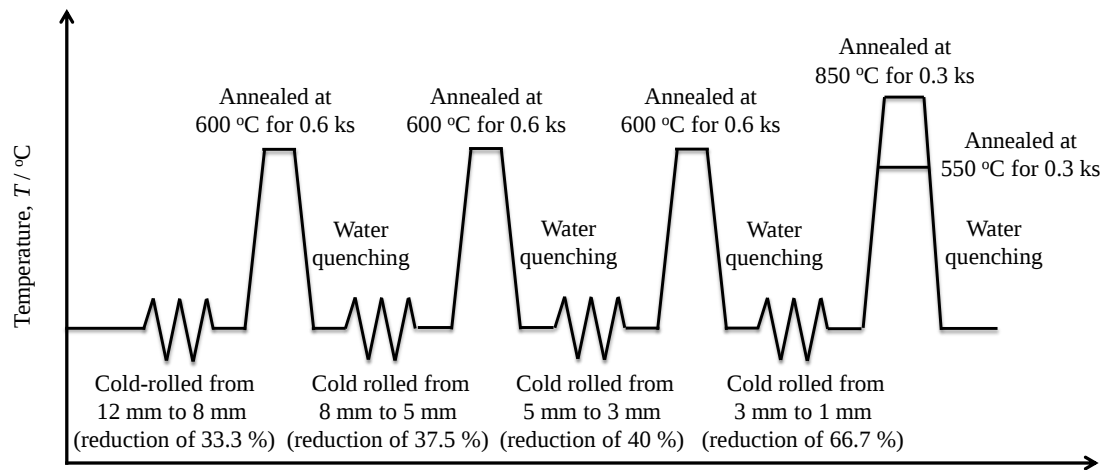


Figure 2.2 Schematic illustration of the thermomechanical process for the 22Mn-0.6C steel.

2.2.2 Microstructural characterization

The microstructures of the specimens were characterized by a field emission-scanning electron microscope (FE-SEM, JEOL, JSM-7800F) equipped with a back-scattered electron (BSE) detector and a FE-SEM (JEOL, JSM-7100F) equipped with an electron backscattering diffraction (EBSD) system both operated at an accelerating voltage of 15 kV. The EBSD scanning data were collected by TSL OIM system and analyzed by TSL OIM software. The samples for the SEM-BSE and SEM-EBSD observations were mechanically polished with emery papers and then electro-polished in a solution of 90 vol. % ethanol + 10 vol. % perchloric acid at room temperature with a voltage of 30 V for 30 s. All the microstructures were observed on longitudinal sections perpendicular to the transverse direction (TD) of the cold-rolled

and subsequently heat-treated sheets.

2.3 Results and discussion

2.3.1 Effect of annealing temperature on the grain size in 31Mn-3Al-3Si steel

Figure 2.4 shows a TEM image of the 31Mn-3Al-3Si steel cold-rolled to a reduction of 92 % [5]. The cold-rolled specimen exhibits a lamellar boundary structure elongated along the rolling direction (RD) of the sheet. The mean lamellar spacing is approximately 40 nm.

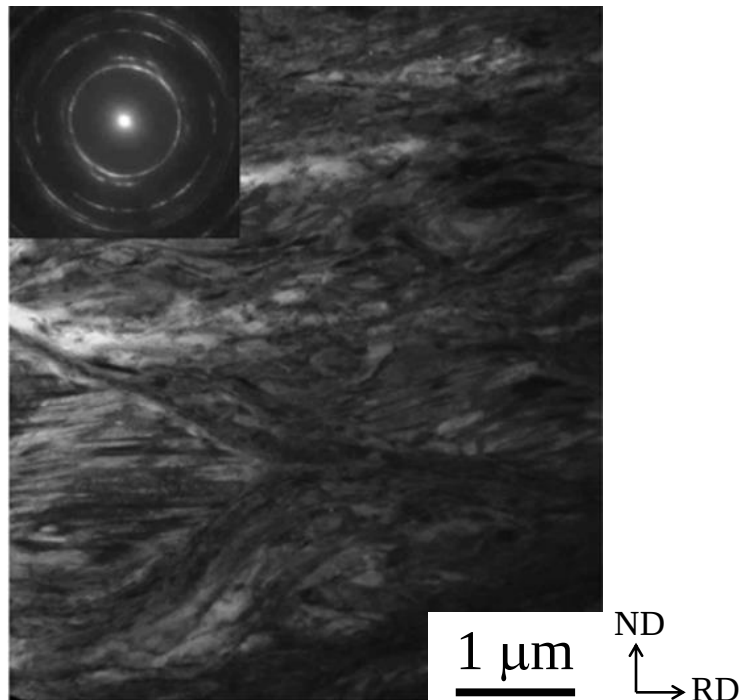


Figure 2.4 TEM image of the 31Mn-3Al-3Si steel cold-rolled to 92 % reduction in thickness [5]. Observed from TD.

Figure 2.5 shows SEM-BSE images of the specimens cold-rolled and subsequently heat-treated at temperatures ranging from 650 °C to 1000 °C for various periods. All the microstructures show equiaxed grains, indicating that they were fully recrystallized. **Figure 2.6** shows EBSD grain boundary maps of the different grain-sized specimens that correspond to the microstructures shown in **Figure 2.5**. Low angle boundaries ($2^\circ \leq \theta < 15^\circ$), high angle boundaries ($15^\circ \leq \theta$) and annealing twin boundaries ($\Sigma 3$) are indicated by green, black and red lines, respectively. All the microstructures exhibit fully-recrystallized structures with a large amount of annealing twins. The mean grain size measured by using the linear interception method on the EBSD grain boundary maps are summarized in **Table 2.3**.

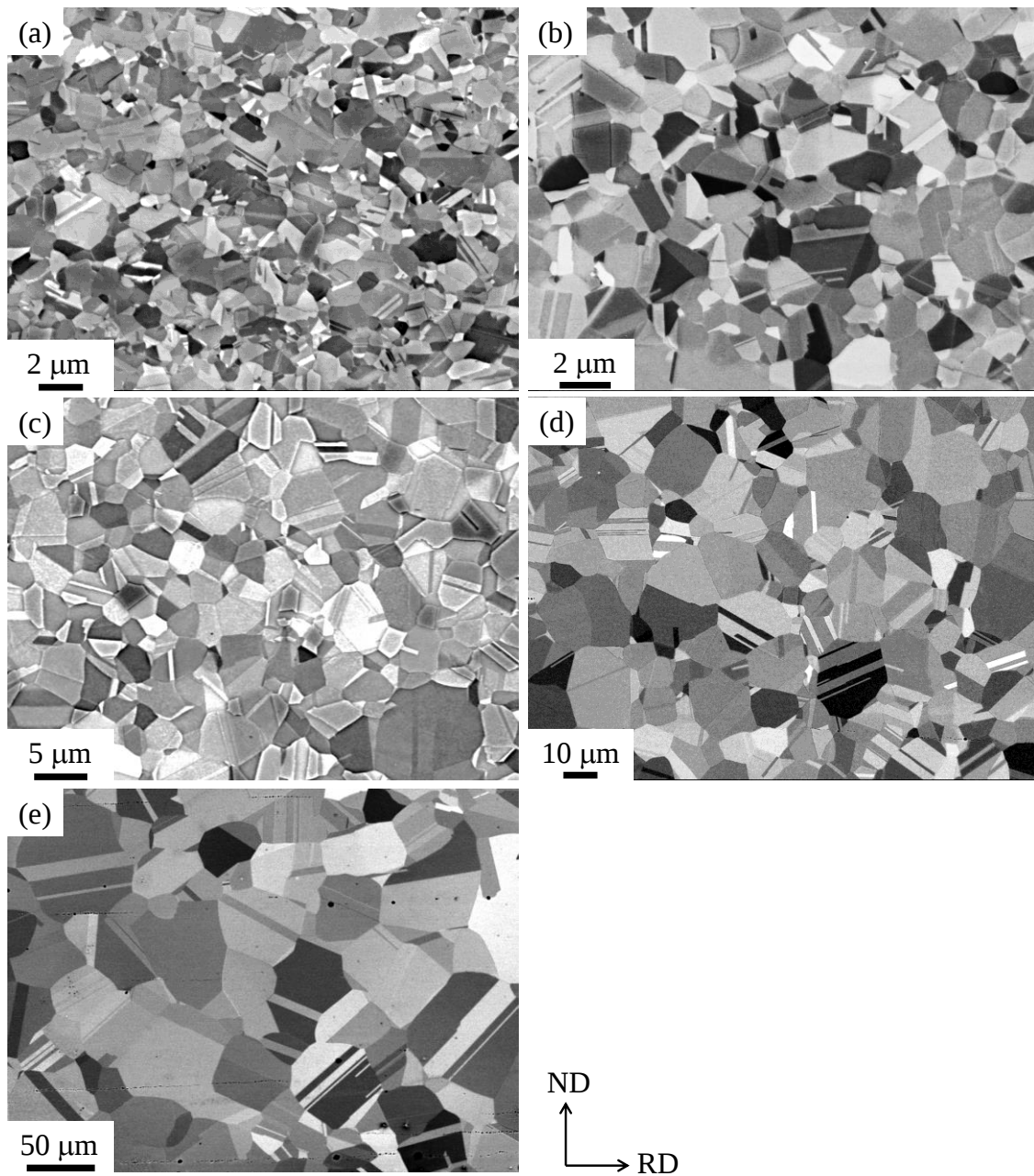


Figure 2.5 SEM-BSE images showing microstructures of the 31Mn-3Al-3Si steel cold-rolled and subsequently heat-treated at different temperatures for various periods: (a) 650 °C for 0.3 ks, (b) 725 °C for 0.3 ks, (c) 800 °C for 0.3 ks, (d) 900 °C for 0.3 ks, and (e) 1000 °C for 1.8 ks.

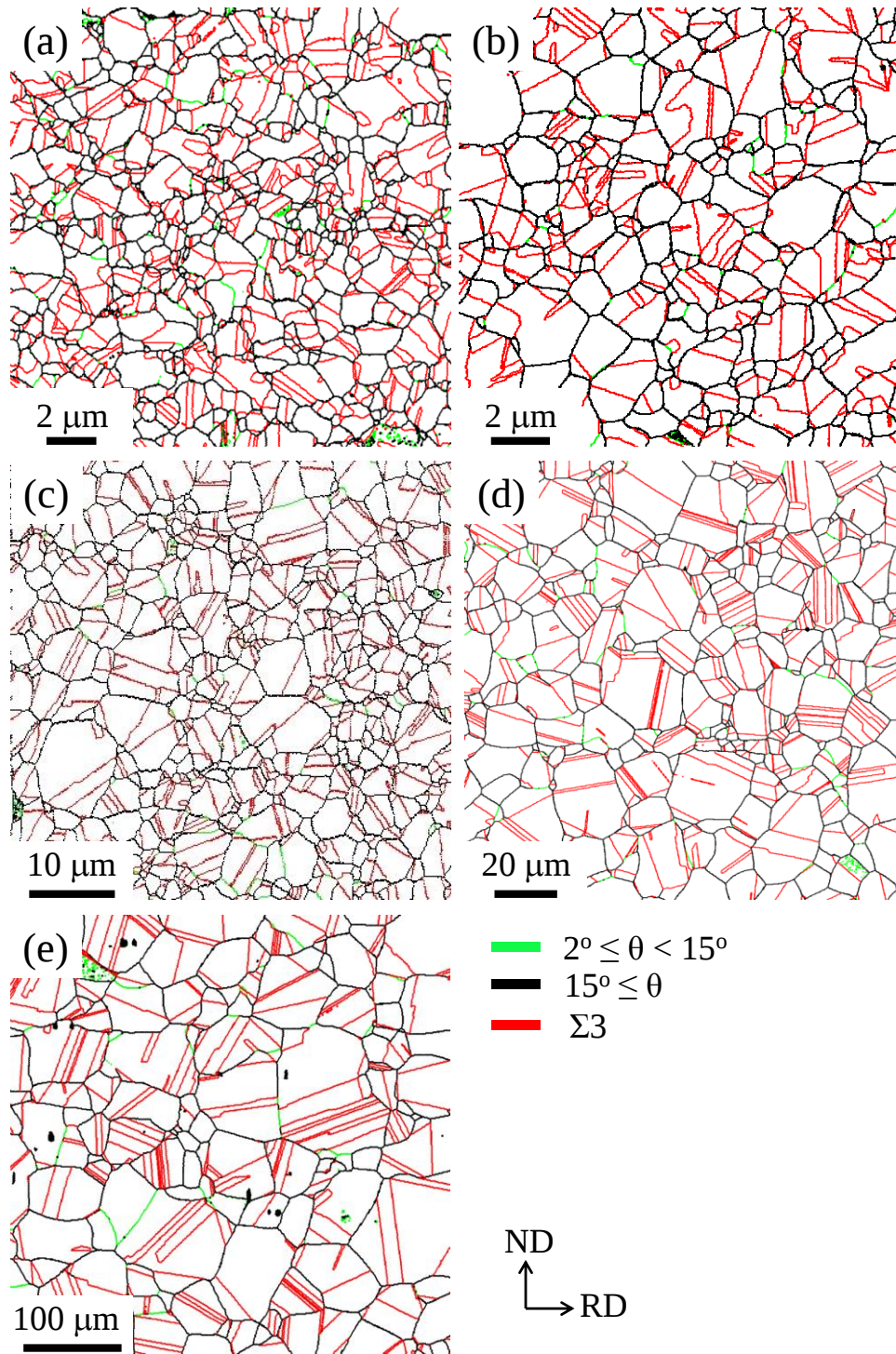


Figure 2.6 EBSD grain boundary maps of the 31Mn-3Al-3Si steel cold-rolled and subsequently heat-treated at different temperatures for various periods. The green, black and red lines correspond to low-angle grain boundaries ($2^\circ \leq \theta < 15^\circ$), high-angle grain boundaries ($15^\circ \leq \theta$), and twin boundaries ($\Sigma 3$), respectively. (a) 650 °C for 0.3 ks, (b) 725 °C for 0.3 ks, (c) 800 °C for 0.3 ks, (d) 900 °C for 0.3 ks, and (e) 1000 °C for 1.8 ks.

Table 2.3 Summary of the grain sizes obtained after different annealing temperatures in the 31Mn-3Al-3Si steel.

Annealing temperature		650 °C	725 °C	800 °C	900 °C	1000 °C
Grain size (µm)	Including annealing twins	0.56	0.78	1.5	4.9	19
	Excluding annealing twins	0.84	1.0	2.3	9.9	37

Figure 2.7 shows distribution profiles of the boundary misorientation obtained by EBSD analysis in the specimens with various grain sizes (**Figure 2.6**). In all cases, the fraction of low angle boundary was relatively small. There are large peaks at the misorientation around 60° in all the different grain-sized specimens, indicating presence of large fraction of annealing twin boundaries. The fraction of annealing twin boundaries in each grain-sized specimen is indicated in each graph of **Figure 2.6**. The fraction of annealing twin boundaries was more than 29 % in all the cases and the fraction tends to increase with increasing the grain size.

Figure 2.8 shows the mean grain sizes including annealing twin boundaries as a function of the annealing temperature of the cold-rolled 31Mn-3Al-3Si steel. The smallest grain size, 0.56 µm, was obtained at the lowest annealing temperature of 650

°C. With increasing the annealing temperature from 725 °C to 1000 °C, grain size increased from 0.78 μm to 19 μm .

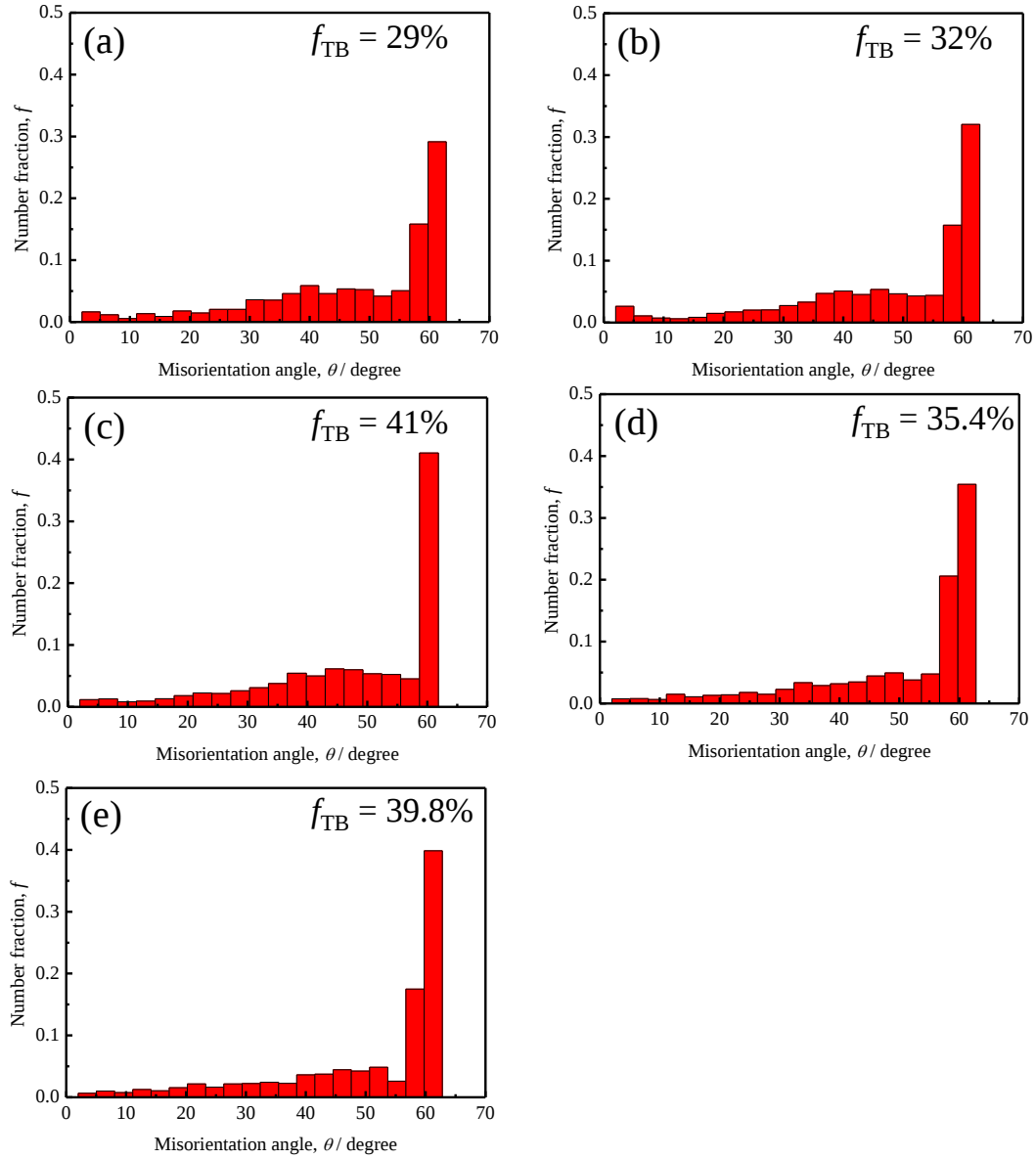


Figure 2.7 Misorientation distributions obtained by EBSD analysis in the specimens corresponding to the observation areas shown in **Figure 2.6**: (a) annealed at 650 °C for 0.3 ks, (b) annealed at 725 °C for 0.3 ks, (c) annealed at 800 °C for 0.3 ks, (d) annealed at 900 °C for 0.3 ks, and (e) annealed at 1000 °C for 1.8 ks.

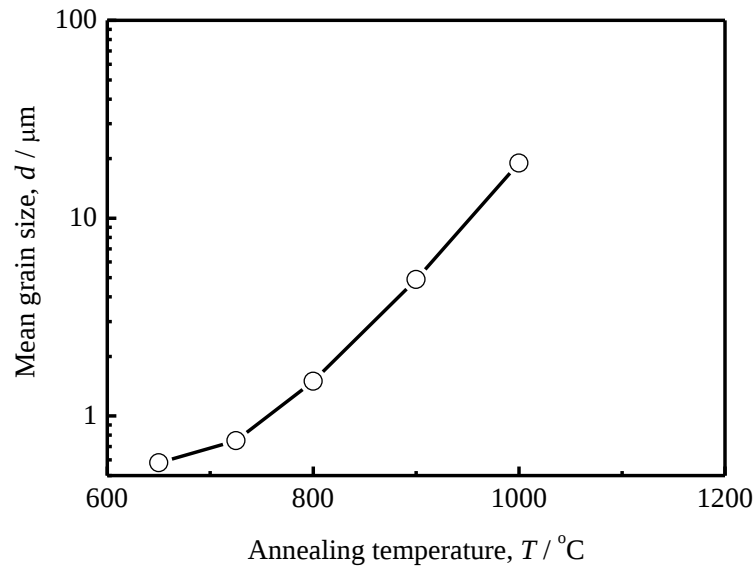


Figure 2.8 Mean grain sizes of the specimens of 31Mn-3Al-3Si cold-rolled by 92 % and subsequently annealed at different temperatures ranging from 650 °C to 900 °C for 0.3 ks or at 1000 °C for 1.8 ks.

2.3.2 Effect of reduction in cold rolling on the grain size in 22Mn-0.6C steel

Firstly, the same method as that applied in the 31Mn-3Al-3Si steel, i.e., conventional multi-pass cold rolling and annealing, was applied to the 22Mn-0.6C steel to fabricate ultrafine grains. As shown in **Figure 2.9**, however, large cracks generated from side edges of the sheet and significantly propagated toward the center after cold-rolled to a total reduction of 92 %. This is because the hardness of the starting materials is higher in the 22Mn-0.6C steel than that in the 31Mn-3Al-3Si steel, and the deformability of the 22Mn-0.6C steel is originally not good. With increasing strains

by cold rolling, the hardness of the 22Mn-0.6C steel increased significantly. As a result, further deformation at room temperature became difficult to continue and crack generated. Therefore, it was difficult to fabricate ultrafine grains in the 22Mn-0.6C steel by the same process as that for the 31Mn-3Al-3Si steel. Then, annealing treatment was carried out to relieve stresses and decrease hardness after certain degree of cold rolling process, so that further deformation during cold rolling would become easier. As introduced in **Figure 2.3**, cold rolling and subsequent annealing process was repeated for four times to fabricate ultrafine grains in the 22Mn-0.6C steel.

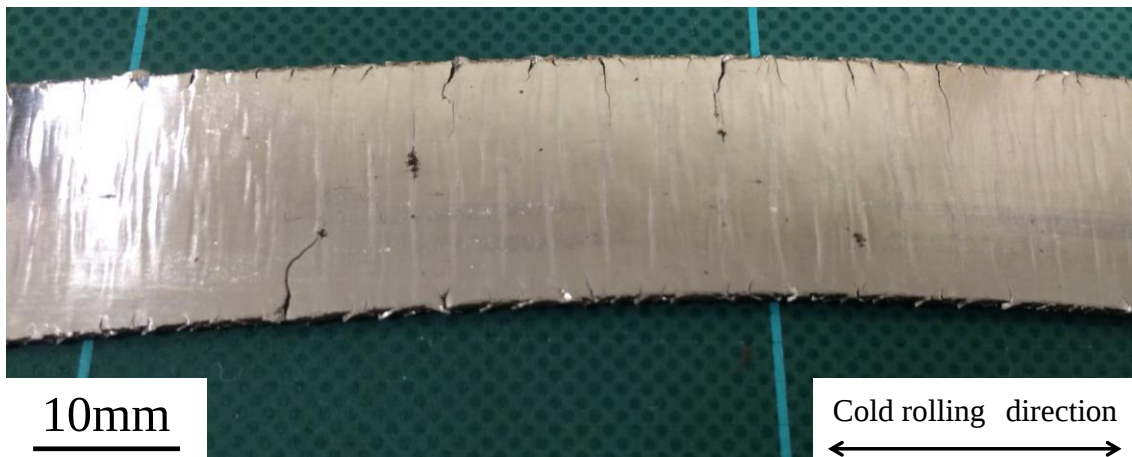


Figure 2.9 Appearance of the cold-rolled sheet of 22Mn-0.6C with a total reduction of 92 %.

Figure 2.10 shows SEM-BSE images of deformation microstructures of the as-cold-rolled specimens of 22Mn-0.6C before annealing process in each step. The cold rolling reduction in each step is indicated in each image. All the as-cold-rolled

specimens showed lamellar microstructures elongated along the cold rolling direction. After the cold rolling with a reduction of 33.3 % in the first step (**Figure 2.10 (a)**), a large amount of deformation twins were observed. However, deformation was not homogenous and areas with smooth microstructures also existed (like the region surrounded by a thin black line), which was probably due to the small amount of cold rolling reduction (33.3%). After cold rolling with a reduction of 37.5 % in the second step (**Figure 2.10 (b)**) and that with a reduction of 40 % in the third step (**Figure 2.10 (c)**), the deformed microstructure was refined, and deformation microstructure became more homogenous. After the cold rolling with a reduction of 66.7 % in the fourth (last) step (**Figure 2.10 (d)**), the deformation microstructure became very fine and homogenous.

Figure 2.11 shows EBSD grain boundary maps of the specimens after annealing in each step. The cold rolling and annealing conditions in each step are indicated in the figures. After the first step (33.3 % cold rolling reduction and annealing at 600 °C for 0.6 ks), the microstructure consisted of fine grains and unrecrystallized coarse grains (**Figure 2.11 (a)**). After the second step (37.5 % cold rolling reduction and annealing at 600 °C for 0.6 ks) and third step (40 % cold rolling reduction and annealing at 600 °C for 0.6 ks), the microstructures became fully recrystallized, and the grain size decreased

significantly and grain size distributions became more homogenous (**Figure 2.11** (b, c)).

Note that a large number of annealing twins were observed in each specimen.

However, the grain size was still around several micrometers. After the last step (66.7 %

cold rolling reduction and annealing at 550 °C for 0.3 ks), fully recrystallized ultrafine

grains were obtained. Another specimen with fine grains was also fabricated through

annealing at 850 °C in the last step. The microstructure of the specimens obtained

after the last (fourth) step would be discussed in the next paragraph.

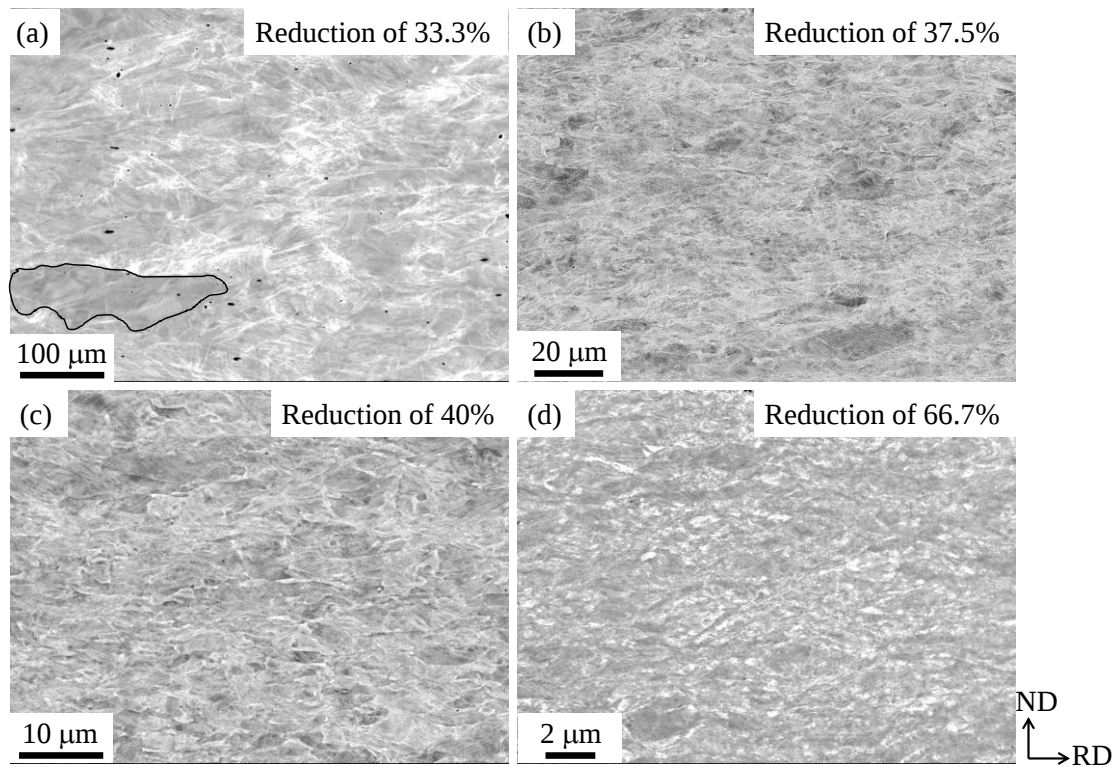


Figure 2.10 SEM-BSE images showing deformation microstructures of the as-cold-rolled samples in the 22Mn-0.6C steel before annealing at each step of the fabrication process: (a) in the first step with a cold-rolling reduction of 33.3 %, (b) in the second step with a reduction of 37.5 %, (c) in the third step with a reduction of 40 %, and (d) in the fourth step with a reduction of 66.7 %.

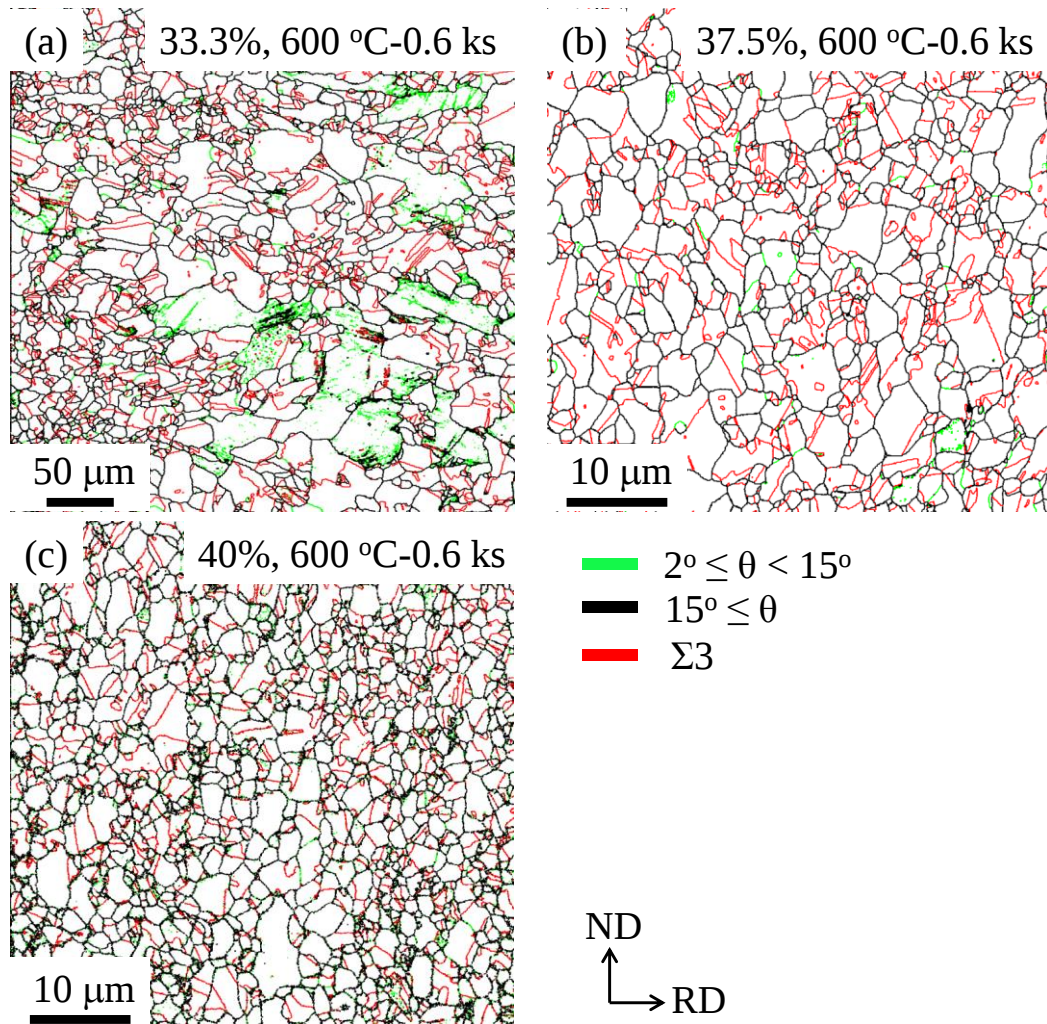


Figure 2.11 EBSD grain boundary maps of the specimens of 22Mn-0.6C steel cold-rolled and annealed in each step. The cold rolling reductions and annealing temperatures at each step are indicated in the figures: (a) after the first step, (b) after the second step, and (c) after the third step of the thermomechanical process.

Figure 2.12 shows SEM-BSE images of the starting material and the specimens after four steps of cold-rolling and annealing processes. All the microstructures show equiaxed grains, which indicates that they were fully-recrystallized. The EBSD grain boundary maps of the specimens are shown in **Figure 2.13**. Low angle boundaries (2°

$\leq \theta < 15^\circ$), high angle boundaries ($15^\circ \leq \theta$) and annealing twin boundaries ($\Sigma 3$) are indicated by green, black and red lines, respectively. A large number of annealing twins were observed in each grain-sized specimen. The mean grain sizes measured from **Figure 2.13** are summarized in **Table 2.4**. The grain size decreased with decreasing the annealing temperature at the last step of the fabrication process. The distribution profiles of boundary misorientation obtained by EBSD analysis of each grain-sized specimen are shown in **Figure 2.14**. The fractions of annealing twin boundaries are indicated in each figure. The results indicate that the amount of annealing twins keeps constant and does not depend on the grain size.

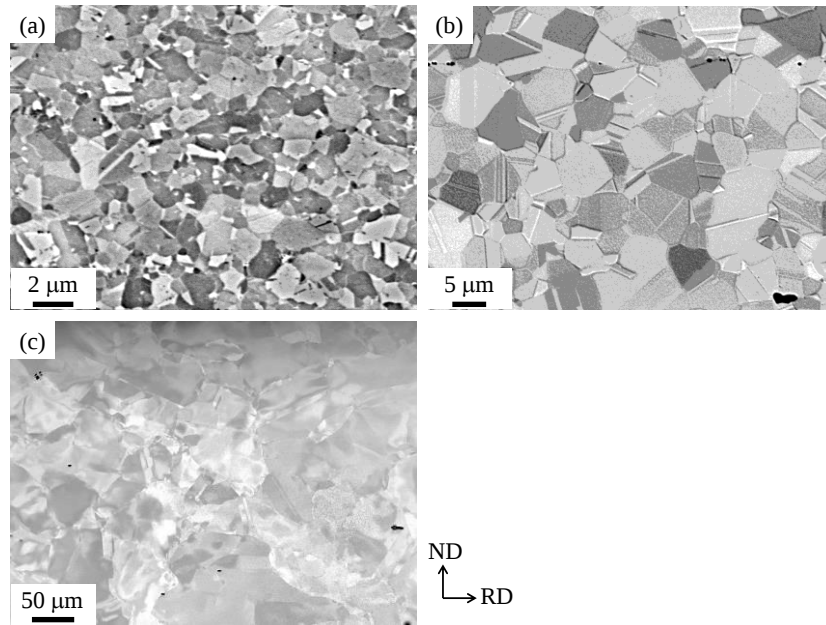


Figure 2.12 SEM-BSE images of the specimens after the four-step cold-rolling and subsequent annealing and the starting material in the 22Mn-0.6C steel: (a) annealed at 550 °C for 0.3 ks in the last step, (b) annealed at 850 °C for 0.3 ks in the last step, and (c) starting material.

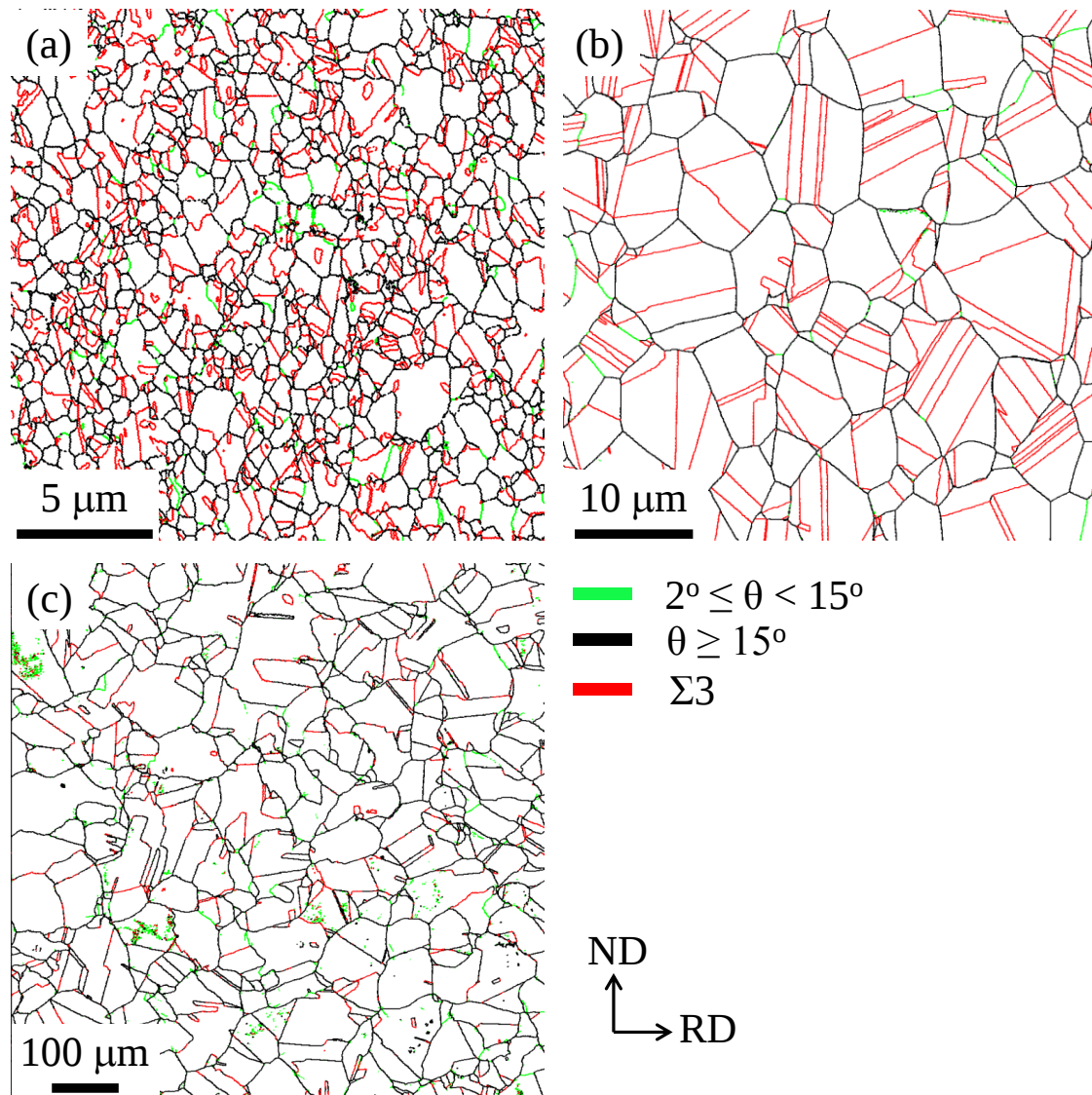


Figure 2.13 EBSD grain boundary maps of the specimens after the four-step cold-rolling and subsequently annealing and the starting material: (a) annealed at 550 °C for 0.3 ks in the last step, (b) annealed at 850 °C for 0.3 ks in the last step, and (c) starting material.

Table 2.4 Summary of the grain sizes of the 22Mn-0.6C steel processed at different annealing temperatures in the last step of the thermomechanical process.

Annealing temperature	550 °C	850 °C	Starting material
Grain size size (μm)	0.58	2.4	21
	0.69	5.0	44

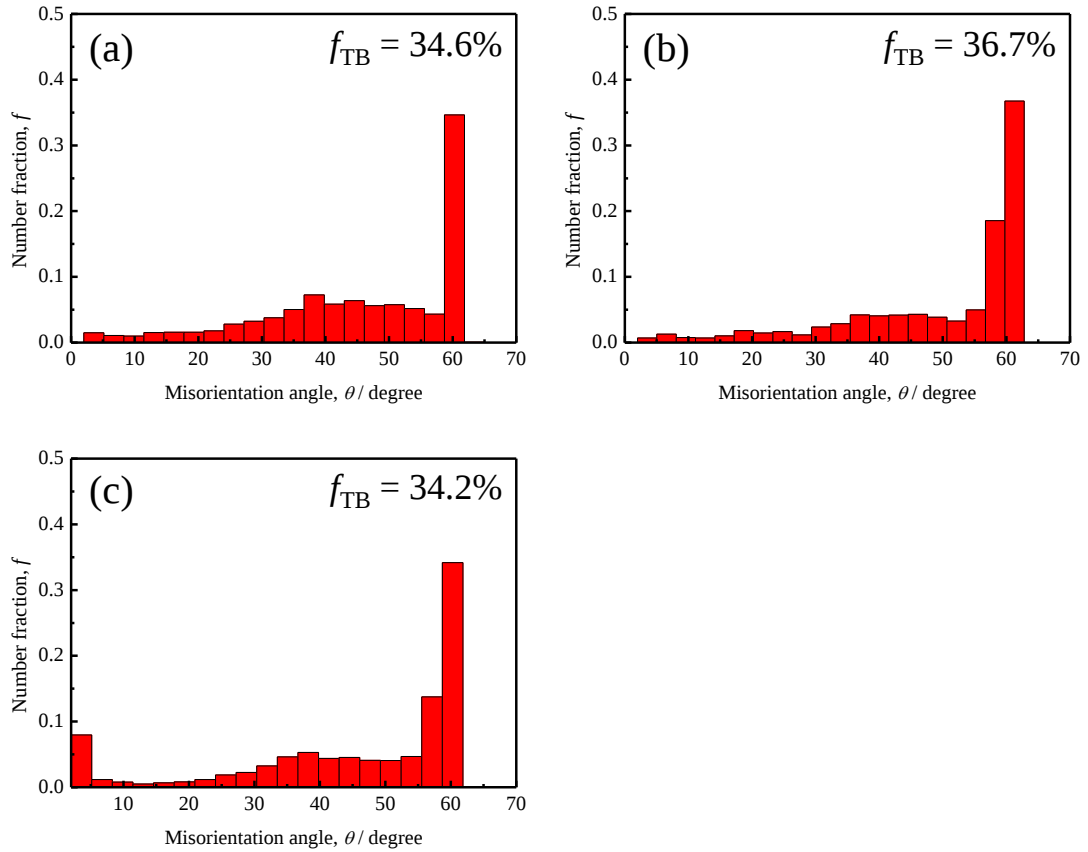


Figure 2.14 Misorientation distributions obtained by EBSD analysis in the specimens having different grain sizes: (a) annealed at 550 °C for 0.3 ks in the last step ($d = 0.58 \mu\text{m}$), (b) annealed at 850 °C for 0.3ks in the last step ($d = 2.4 \mu\text{m}$), and (c) starting material ($d = 21 \mu\text{m}$).

It has been reported that deformation twinning would enhance grain refinement in a Cu-Zi alloy having a low stacking fault energy [6]. With increasing applied strain, the initial grains were subdivided gradually to ultrafine grains by grain subdivision mechanism and deformation twins enhanced grain subdivision. The formed deformation twins were further subdivided by the other variants of twins. The same grain refinement mechanism would occur in high-manganese austenitic steels during SPD processes or heavy cold rolling processes. As a result, the deformed microstructures of the material include high dislocation density and large number of potential nuclei for recrystallization, so that ultrafine-grained microstructure could be fabricated. Accordingly, as seen in the present research, the 31Mn-3Al-3Al and 22Mn-0.6C steels with fully recrystallized ultrafine-grained structures of which mean grain sizes were much smaller than 1 μm could be obtained by conventional cold rolling and subsequent annealing processes.

2.4 Conclusions

In this chapter, various grain-sized high-manganese austenitic steels, F-31Mn-3Al-3Si and Fe-22Mn-0.6C, were fabricated by cold rolling and subsequent heat treatment. Without severe plastic deformation, a fully-recrystallized microstructure with a grain size of 0.56 μm was successfully achieved by conventional multi-pass cold rolling and subsequent annealing at 650 °C in the 31Mn-3Al-3Si steel. A fully recrystallized microstructure with a grain size of 0.58 μm was also fabricated by four-step cold rolling and subsequent annealing the in the 22Mn-0.6C steel. The results obtained in this chapter are summarized below.

1. Fully recrystallized specimens with various mean grain sizes were obtained by conventional multi-pass cold rolling by 92 % reduction and subsequent annealing in the 31Mn-3Al-3Si steel without severe plastic deformation. The obtained mean grain sizes of the cold-rolled and subsequently heat-treated specimens ranged from 19 μm to 0.56 μm , and the grain size decreased with decreasing the annealing temperature from 1000 °C to 650 °C.
2. Ultrafine-grained specimens with fully recrystallized microstructures were obtained by four-step cold rolling and subsequent annealing in the 22Mn-0.6C steel. The grain size was determined by the final annealing temperature, and the minimum

grain size of 0.58 μm could be obtained through annealing at 550 $^{\circ}\text{C}$ in the last step.

2.5 References

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Chapter 3 Hydrogen embrittlement behaviors of various grain-sized 31Mn-3Al-3Si austenitic steel

3.1 Introduction

As mentioned in **Chapter 1**, some researches about hydrogen embrittlement in various high-manganese austenitic steels with typical chemical compositions have already been published in recent years [1-5]. However, any researches on hydrogen embrittlement behaviors in a 31Mn-3Al-3Si steel, one of the typical high-manganese austenitic steels, cannot be found. The 31Mn-3Al-3Si steel exhibits outstanding mechanical properties of very large tensile elongation and high strength. However, the yield strength of this high-manganese austenitic steel is lower than the other high-manganese austenitic steels, since it is a single-phase austenitic (FCC) steel without carbon. To modify the weakness of the lower strength of Mn-Al-Si high-manganese austenitic steels, the grain refinement was applied to enhance the strength without changing the chemical composition. Generally, hydrogen embrittlement susceptibility increases with increasing the strength [6]. Consequently, hydrogen embrittlement might be one of the serious problems for practical use of the materials with fine grains or ultrafine grains.

The effect of grain size on the hydrogen embrittlement in a precipitation strengthened Fe-Ni based austenitic alloy has been investigated [7]. The result indicated that hydrogen embrittlement sensitivity was reduced by decreasing the grain size. However, the grain sizes studied were between 32 μm and 95 μm , which were still coarse grain sizes. As introduced in **Chapter 2**, grain size of a 31Mn-3Al-3Si steel can be changed from coarse grain scale to ultrafine grain scale by a combination of conventional cold rolling and subsequent annealing. However, there is no research investigating the effect of grain size on hydrogen embrittlement behaviors in Mn-Al-Si steels with ultrafine-grained microstructures.

This chapter aims to investigate the effect of grain size on the hydrogen embrittlement of the 31Mn-3Al-3Si austenitic steel, and to discuss the relationship between the grain size and the tensile fracture behaviors including fracture morphology.

3.2 Experimental procedure

3.2.1 Material

A 31Mn-3Al-3Si austenitic steel (wt. %) was used in this study. The chemical composition of the high-manganese austenitic steel is listed in **Table 2.1** shown in **Chapter 2**. The SFE (stacking fault energy) of this material with a coarse grain size ($d = 19 \mu\text{m}$) has been calculated to be less than $43 \text{ mJ} / \text{m}^2$ according to a thermodynamic model in a previous literature [8].

3.2.2 Hydrogen pre-charging

Hydrogen was pre-charged by a cathodic electro-charging method. A schematic illustration of this method is shown in **Figure 3.1**. One end of the specimen was covered with thread seal tape and was connected to the cathodic side. Platinum plate was used as anode and one end of the platinum plate was also covered with thread seal tape. The other ends of the specimen and Pt plate not covered with the tape were immersed in the hydrogen charging solution. The hydrogen charging solution covers the exposed parts of the specimen and the Pt plate.

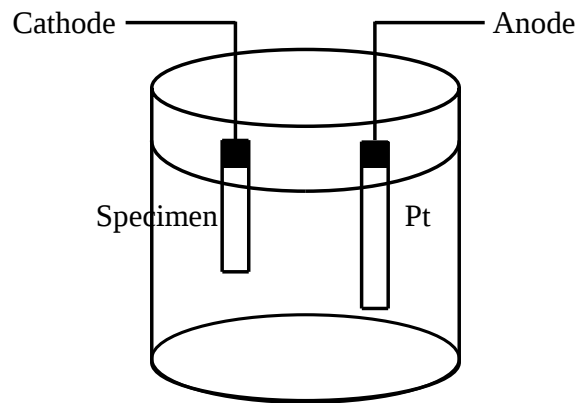


Figure 3.1 Schematic illustration of the cathodic hydrogen charging method used in the present study.

Hydrogen was introduced into the tensile test specimens in a 3% NaCl + 3 g / L NH_4SCN aqueous solution with a current density of $100 \text{ A} / \text{m}^2$ for 172.8 ks (48 hr). The cathodic hydrogen charging method involves three steps [9]: (1) hydrogen discharge reaction, (2) hydrogen recombination reaction (either by chemical recombination or electrical desorption), and (3) hydrogen permeation into the specimen. Hydrogen atoms accumulate at the surface of the specimen, which is the cathodic side, during the hydrogen discharge reactions. The hydrogen atoms tend to recombine to hydrogen molecules and to be released to the environment. Hydrogen permeating into the bulk materials during cathodic charging is only in the form of atom [10]. In order to prevent the recombination reaction and promote the hydrogen absorption into the specimen, a small amount of NH_4SCN was added in the hydrogen charging solution.

3.2.3 Diffusible hydrogen content measurement

The hydrogen content was measured by thermal desorption gas spectroscopy (TDS) using a TDS equipment (J-Science lab, JTF-20A) at a constant heating rate of 100 °C / hr from room temperature to 800 °C. The tensile test specimen was hydrogen-charged and the gauge part was cut out immediately after hydrogen charging. And then the TDS measurement was carried out. In order to keep the amount of hydrogen that escaped from the hydrogen-charged specimens to the environment the same in the hydrogen-charged specimens, the TDS measurement was accurately started 1.8 ks after the hydrogen charging process was finished. In the TDS measurement, the hydrogen released from the specimen was analyzed by a gas chromatography using standard argon carrier gas mixed with hydrogen gas. The sample gas was analyzed in sequential 5 min intervals.

3.2.4 Diffusible hydrogen distribution

Hydrogen has relatively slow diffusivity in austenitic steels with FCC structure compared with BCC ferritic steels. In order to measure the hydrogen diffusion distance after hydrogen charging, the surface layer of the hydrogen-charged specimens was removed by mechanical polishing by thickness of 5 μm or 10 μm from both sides of the sheet specimen immediately after hydrogen charging. After removing the surface layer, the TDS measurement for the specimens of which surface layers were removed was carried out.

3.2.5 Slow strain rate tensile test

Hydrogen embrittlement behaviors were evaluated by uniaxial slow strain rate tensile test at a crosshead speed of 5×10^{-3} mm / min, corresponding to an initial strain rate of 8.3×10^{-6} / s on a tensile test machine (Shimadzu, AG-X plus, 100 kN) using the specimens with 10 mm length and 5 mm width in the gauge part. The detailed dimensions of the tensile test specimen are shown in **Figure 3.2**. The tensile test specimens were cut from the cold-rolled and subsequently annealed sheet (1 mm thick) by an electro discharge machine (Brother, HS-70A). The surface of the tensile test

specimen was mechanically polished to a thickness of 0.6 mm. In order to keep the surface condition the same in all the hydrogen-charged specimens, the specimen surface was polished by buff before hydrogen charging. Actually, hydrogen started to escape from the specimen surface just after hydrogen charging was completed. To keep the condition the same in every hydrogen-charged specimen for the tensile test, the tensile test was started accurately 1.8 ks after the hydrogen charging process was completed. In order to measure the tensile strain of the specimen precisely, an extensometer (Shimadzu, SG10-100) was attached to the gauge part of the specimen to detect the displacement of the gauge part. The displacement until 0.2 mm could be measured by the extensometer. Beyond the region, the tensile strain was calculated from the displacement of the crosshead. The tensile tests were carried out two times for each uncharged and hydrogen-charged specimen to check the reproducibility.

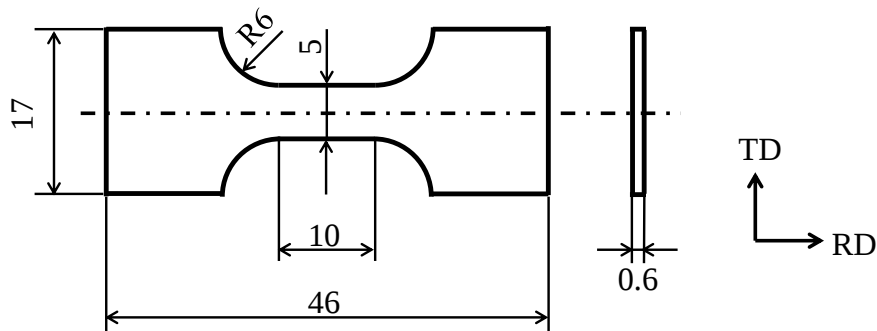


Figure 3.2 Schematic illustration of the tensile test specimen.

3.2.6 Fracture surface observation

The fracture surfaces of the uncharged and hydrogen-charged specimens after tensile fracture were observed by scanning electron microscopy (SEM) using a FE-SEM (JEOL, JSM-7800F) operated at an acceleration voltage of 15 kV.

3.3 Results

3.3.1 Microstructural characterization

As introduced in **Chapter 2**, the 31Mn-3Al-3Si (wt. %) steel having various grain sizes were fabricated. In this chapter, the specimens having three kinds of mean grain sizes were chosen to investigate the effect of the grain size on hydrogen embrittlement behavior, namely 19 μm / 37 μm , 1.5 μm / 2.3 μm and 0.56 μm / 0.85 μm , that were the mean grain sizes including / excluding annealing twins, respectively. Hereafter, the specimens are termed as the coarse-grained, fine-grained, and ultrafine-grained specimen, respectively. The microstructures observed are omitted in this chapter, as they were already shown in **Figure 2.6**.

3.3.2 Diffusible hydrogen content

As introduced in **Chapter 1**, there are two kinds of hydrogen trapped by defects inside the materials, i.e., diffusible and non-diffusible hydrogen. During continuous heating in the TDS measurement, it is believed that hydrogen released at a temperature range of 25-200 $^{\circ}\text{C}$ is diffusible one, while that released at a higher temperature higher than 200 $^{\circ}\text{C}$ is non-diffusible one [11, 12]. The diffusible hydrogen is reported to play

a key role in hydrogen embrittlement [13]. Hence, the present study focused on the diffusible hydrogen content, which was determined as the hydrogen desorbed from room temperature to 200 °C in the TDS measurement.

Figure 3.3 shows the hydrogen desorption rate curves of the various grain-sized uncharged (**Figure 3.3** (a)) and hydrogen-charged (**Figure 3.3** (b)) specimens in the 31Mn-3Al-3Si steel. Solid line, broken line, and dotted line indicate the ultrafine-grained, fine-grained, and coarse-grained specimens, respectively. In **Figure 3.3** (a), diffusible hydrogen was not detected in all uncharged specimens with different grain sizes. In contrast, **Figure 3.3** (b) shows large peaks around 110 °C, indicating that considerable amount of diffusible hydrogen was introduced into the specimens by hydrogen charging in all different grain-sized specimens. The diffusible hydrogen contents of the hydrogen-charged coarse-grained, fine-grained and ultrafine-grained specimens were 3.30 wt ppm, 4.58 wt ppm, and 7.10 wt ppm, respectively. The amount of diffusible hydrogen increased significantly with decreasing the grain size.

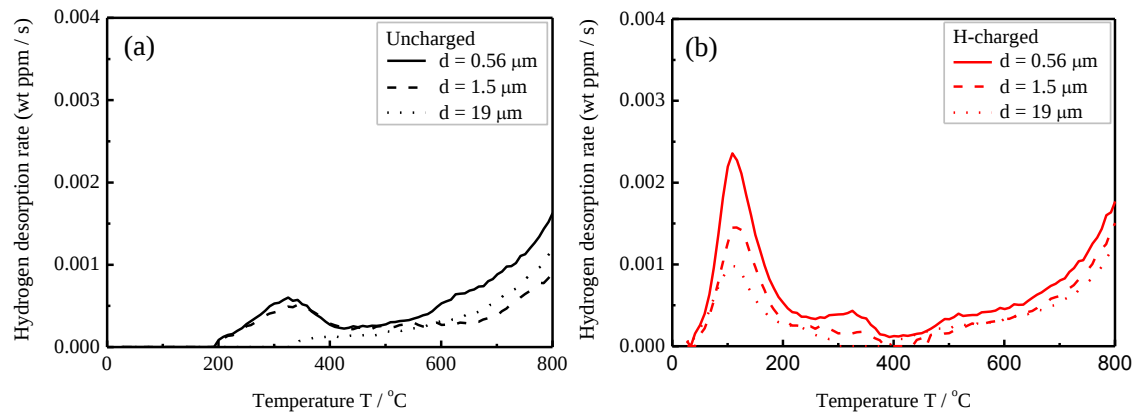


Figure 3.3 Hydrogen desorption rate curves obtained from the TDS measurement of the uncharged (**Figure 3.3 (a)**) and hydrogen-charged (**Figure 3.3 (b)**) samples with various grain sizes. Solid line, broken line, and dotted line indicate ultrafine-grained, fine-grained, and coarse-grained specimens, respectively.

3.3.3 Diffusible hydrogen distribution

It is known that solubility of hydrogen in austenitic steel is relatively large but diffusion of hydrogen is slow in austenite. Considering a diffusion coefficient of hydrogen reported in an austenitic steel at room temperature ($1.29 \times 10^{-13} \text{ m}^2 / \text{s}$ [14]), the diffusion distance of hydrogen is calculated to be around 0.15 mm under the present charging condition (at RT for 48 hr), which is smaller than the half thickness of the specimens (0.3 mm). Therefore, there might be an in-depth gradient of hydrogen distribution in the present specimens, but it should be emphasized that the hydrogen charging was carried out under the identical condition to all the specimens.

Figure 3.4 shows the hydrogen desorption rate curves of the hydrogen-charged specimens after the surface layers were removed from both sides of the specimens by thickness of 5 μm or 10 μm . The results of the hydrogen-charged specimens without removing surface layers are also presented. In all the specimens, the peaks of diffusible hydrogen became smaller after removing the surface layers of 5 μm (as indicated by red lines), and almost no hydrogen was detected after removing the surface layers of 10 μm (as indicated by pink lines). The diffusible hydrogen content in the remnant of the specimens after removing various thicknesses of surface layers is summarized in **Table 3.1**. The result indicates that diffusible hydrogen concentrated within the 10 μm thick surface layer in all the different grain-sized specimens.

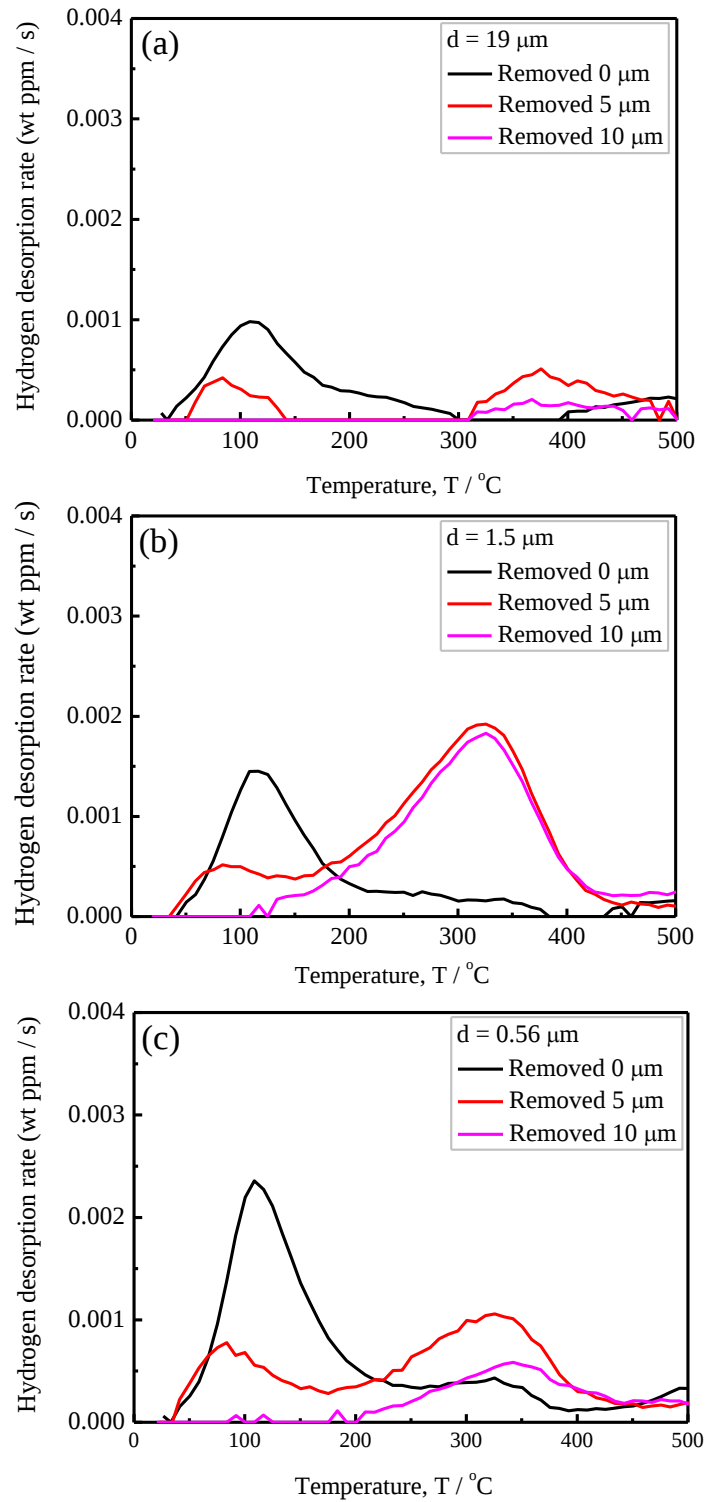


Figure 3.4 Hydrogen desorption rate curves of the hydrogen-charged specimens after removing the surface layers by thickness of 0 μm , 5 μm and 10 μm from both sides: (a) coarse-grained specimens, (b) fine-grained specimens, and (c) ultrafine-grained specimens.

Table 3.1 Summary of diffusible hydrogen contents in the specimens after removing the surface layers by thickness of 0 μm , 5 μm or 10 μm , respectively, from both sides.

Mgrain size, $d / \mu\text{m}$	19			1.5			0.56		
Thickness of removed surface layer, $t / \mu\text{m}$	0	5	10	0	5	10	0	5	10
Diffusible hydrogen content in the remnant of the specimen / wt ppm	3.30	0.84	0	4.58	2.38	0.03	7.10	2.66	0.07

From the values of diffusible hydrogen content and the removed surface layer thickness (**Table 3.1**), the hydrogen concentration profiles were obtained as shown in **Figure 3.5**. The bar indicates the hydrogen concentration within each 5 μm thick layers. It is found from **Figure 3.5** that very high concentration of hydrogen, 120 - 260 wt ppm, existed at the layer with a thickness of 5 μm from the surface. In addition, the hydrogen concentration around the surface increased with decreasing the grain size.

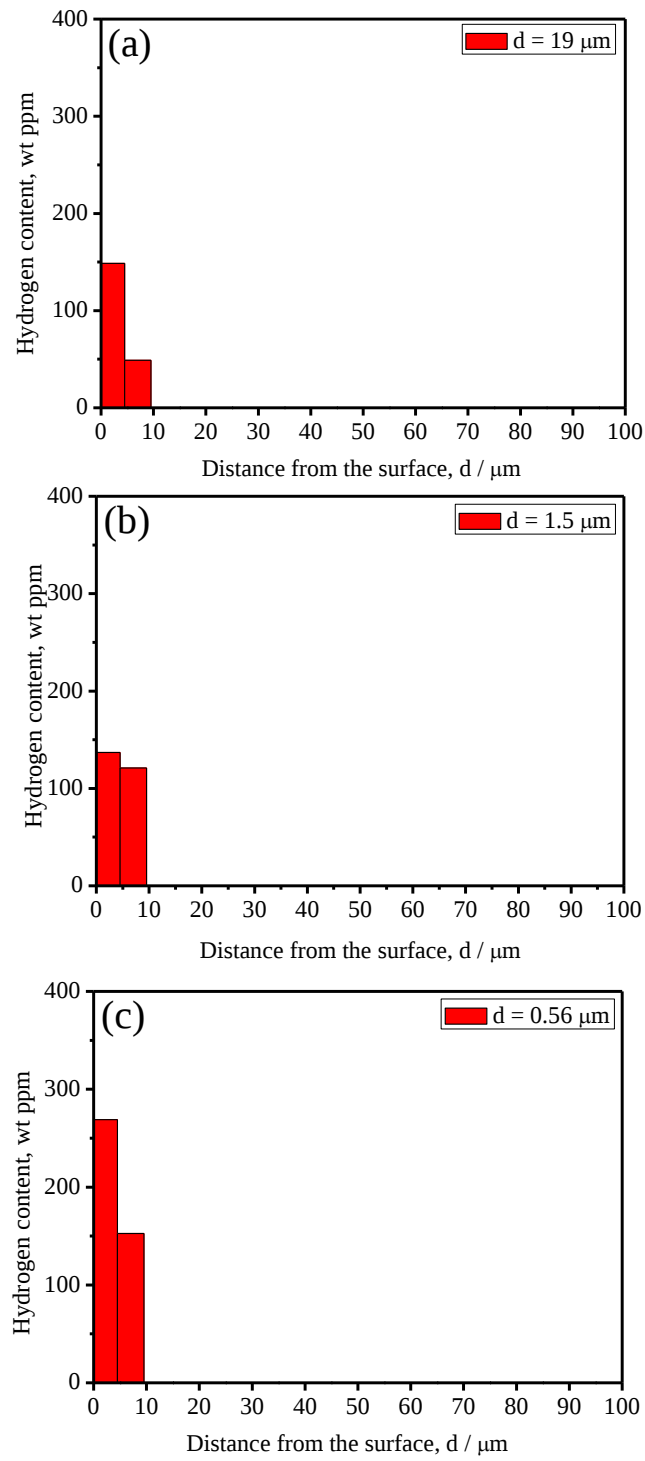


Figure 3.5 Diffusible hydrogen content profiles within each 5 μm surface layer: (a) coarse-grained specimens, (b) fine-grained specimens, and (c) ultrafine-grained specimens.

3.3.4 Mechanical properties

Nominal stress-strain curves of the uncharged and hydrogen-charged specimens with different grain sizes are shown in **Figure 3.6**. The nominal stress-strain curves of the uncharged specimens were indicated by black lines while the hydrogen-charged specimens were indicated by red lines. The grain sizes were also indicated in the figure. The changes of the yield strength, ultimate tensile strength, uniform elongation and total elongation are summarized in **Figure 3.7** and **Table 3.2**. In the uncharged specimens, the yield strength and ultimate tensile strength of the material were greatly enhanced by grain refinement, whereas the total elongation decreased with decreasing the mean grain size. However, the ultrafine-grained specimen still exhibited a large amount of uniform elongation, which is a typical advantage of high-manganese austenitic steels compared with martensitic steels [15]. In addition, the ultrafine-grained specimens exhibited a yield-drop phenomenon, which is often observed in ultrafine-grained materials [16]. Even after hydrogen-charging, the yield strength and the ultimate tensile strength showed no change in each grain-sized specimen compared with the uncharged specimen with the same grain size, as indicated in **Figure 3.7** (a). However, hydrogen-charging gave a certain effect on the tensile elongation (**Figure 3.7** (b)). The total elongation clearly decreased from 118 % to 96 %

in the coarse-grained specimens by hydrogen-charging. Relatively small decrease of total elongation from 70 % to 63 % was observed in the fine-grained specimen, so that the elongation loss became smaller with decreasing the mean grain size. The uniform elongation and total elongation kept almost the same values in the ultrafine-grained specimens regardless of hydrogen-charging. It means that the mechanical properties became less sensitive to hydrogen with decreasing the grain size. The result also indicates that hydrogen-charging has no influence on the yield strength and tensile strength but a significant impact on the tensile elongation in the 31Mn-3Al-3Si steel.

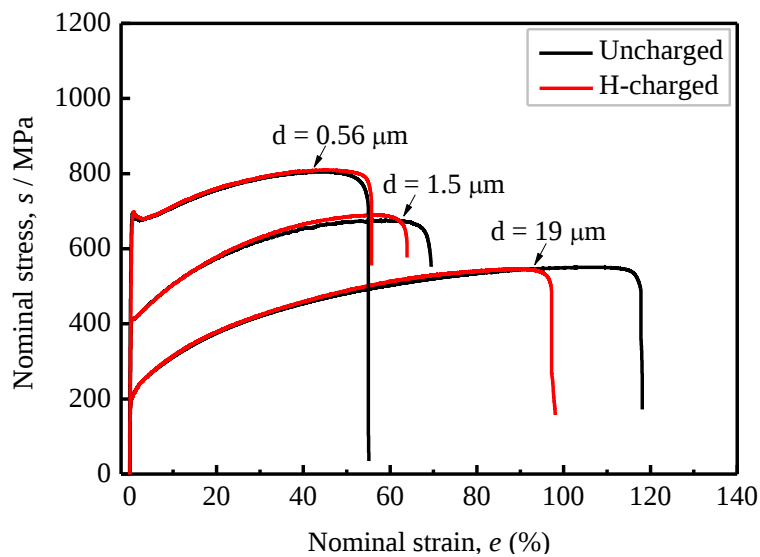


Figure 3.6 Nominal stress-strain curves of the differently grain-sized specimens with and without hydrogen-charging.

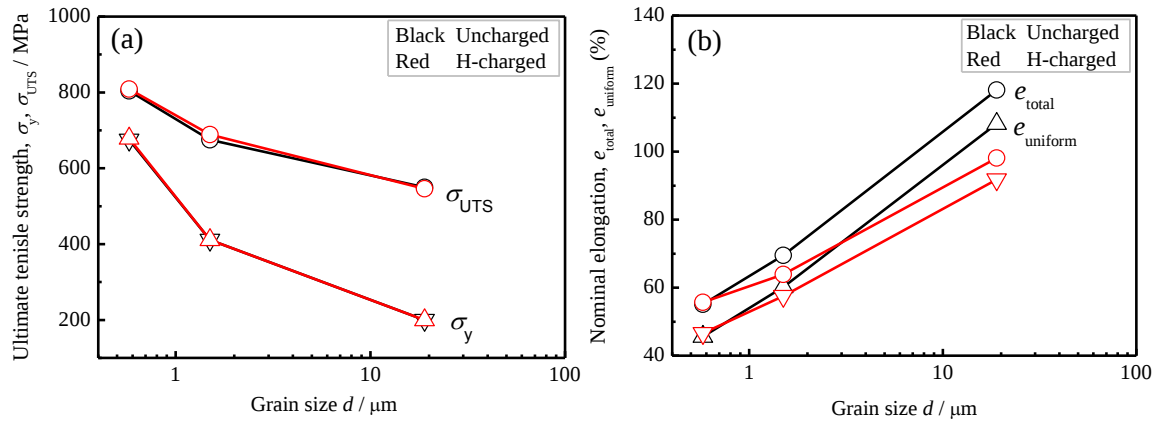


Figure 3.7 Comparison of the tensile properties of the uncharged and hydrogen-charged 31Mn-3Al-3Si steel as a function of mean grain size: (a) the yield strength (σ_y) and ultimate tensile strength (σ_{UTS}); (b) the uniform elongation ($e_{uniform}$) and total elongation (e_{total}).

Table 3.2 Yield strength, ultimate tensile strength, total elongation and uniform elongation obtained from nominal stress-strain curves of the uncharged and hydrogen-charged 31Mn-3Al-3Si specimens with various grain sizes.

Mean grain size, d / μm (include / exclude annealing twins)	Condition	Yield strength, σ_y / Mpa	Ultimate tensile strength, σ_{UTS} / Mpa	Total elongation, e_{total} / %	Uniform elongation, $e_{uniform}$ / %
19 / 37	Uncharged	200	550	118	108
	H-charged	200	546	96	92
1.5 / 2.3	Uncharged	411	675	70	60
	H-charged	411	689	63	58
0.56 / 0.85	Uncharged	675	804	55	46
	H-charged	679	809	56	47

3.3.5 Fracture surface observation

Figures 3.8, 3.9 and 3.10 show the fracture surfaces of the uncharged and

hydrogen-charged specimens with different grain sizes observed by SEM after fracture in the slow strain rate tensile tests. The estimated hydrogen existing distance from the surface under the present hydrogen charging condition was approximately 10 μm in all the hydrogen-charged specimens with different grain sizes. However, no brittle fracture region was observed in the region of 10 μm beneath the surface. The fracture surfaces were mostly covered by dimples in all the specimens regardless of the existence of hydrogen, which were characteristic ductile fracture indicating void nucleation and coalescence. In addition, the dimples became fine and shallow with decreasing the grain size. Comparing the fracture surfaces of the hydrogen-charged specimens with different grain sizes, it is noteworthy that the coarse-grained specimen exhibited some secondary cracks with length larger than 100 μm on the fracture surface (**Figure 3.8** (d)), whereas there are some relatively small cracks in the fine-grained specimen (**Figure 3.9** (d)) and almost no secondary crack was observed in the ultrafine-grained specimen (**Figure 3.10** (d)). In addition, a large number of holes were observed in all the specimens (**Figure 3.8** (b, e), **Figure 3.9** (b, e), **Figure 3.10** (b, e)). The holes are probably traces of dropped inclusions.

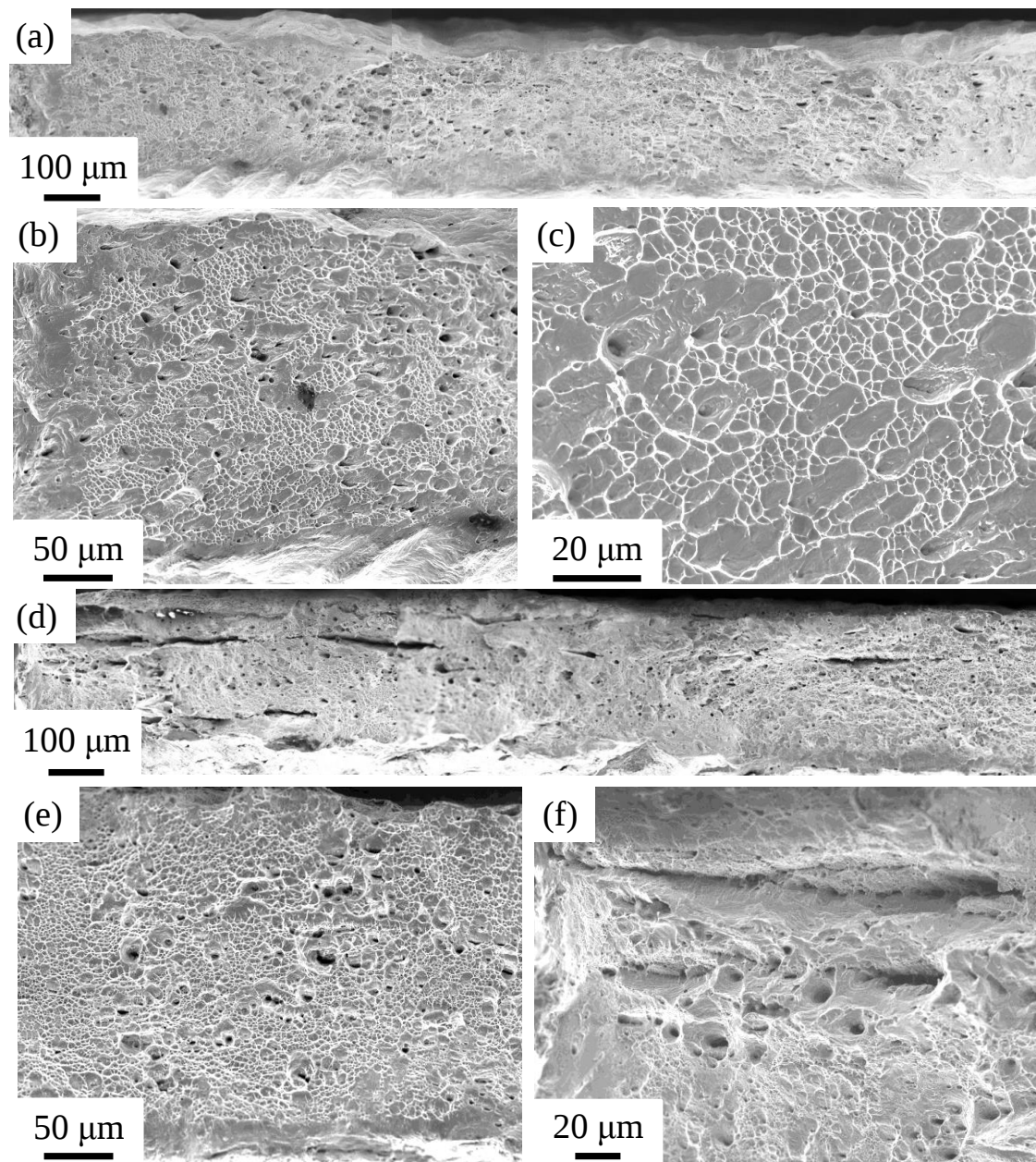


Figure 3.8 Fracture surfaces of the coarse-grained specimens uncharged (a-c) and hydrogen-charged (d-f): (a) is the entire fracture surface of the hydrogen-uncharged specimen, (b) and (c) are the magnified images of (a). (d) is the entire fracture surface of the hydrogen-charged specimen, (e) and (f) are the magnified images of (d).

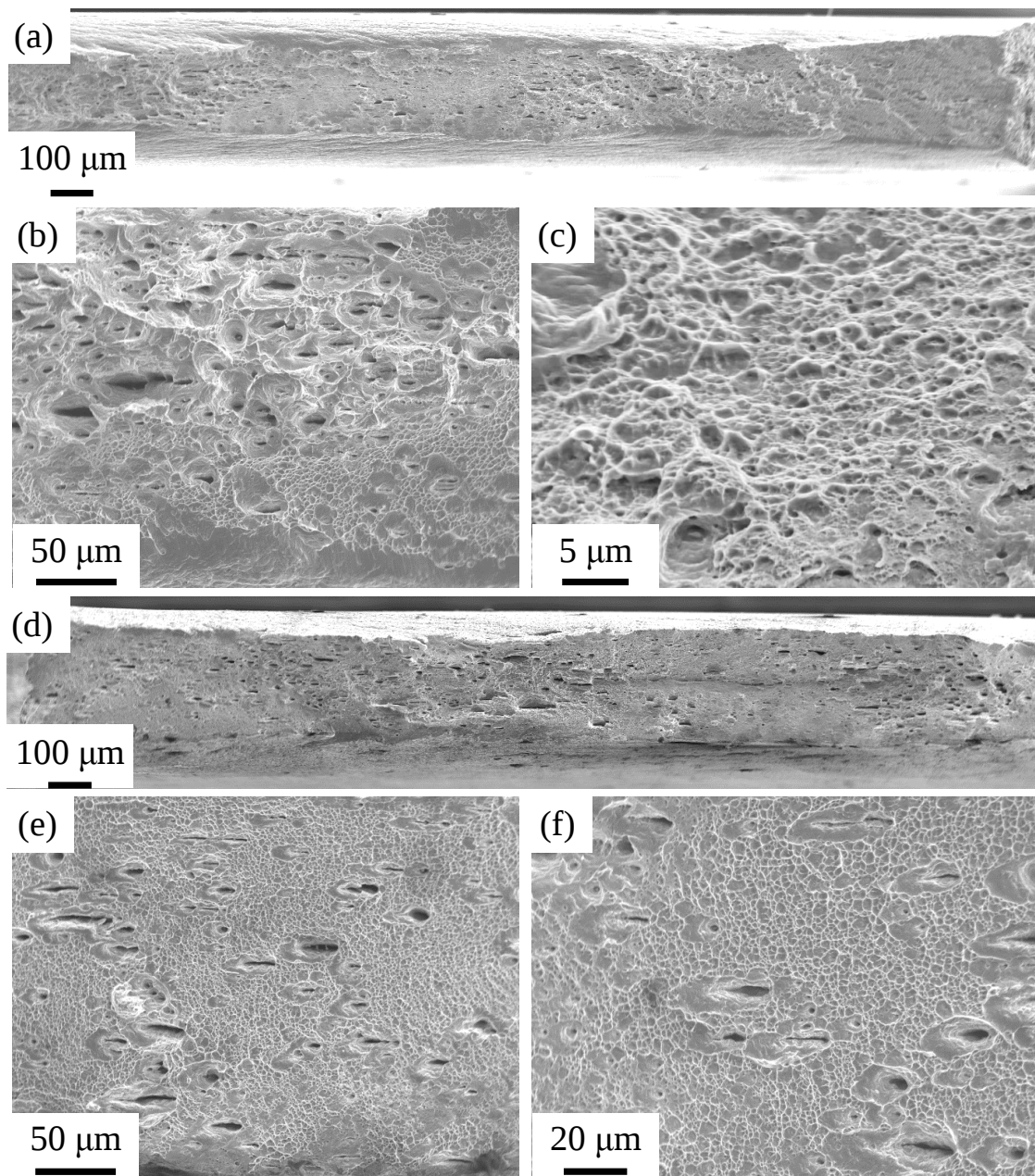


Figure 3.9 Fracture surfaces of the fine-grained specimens with uncharged (a-c) and hydrogen-charged (d-f): (a) is the entire fracture surface of the hydrogen-uncharged specimen, (b) and (c) are the magnified images of (a). (d) is the entire fracture surface of the hydrogen-charged specimen, (e) and (f) are the magnified images of (d).

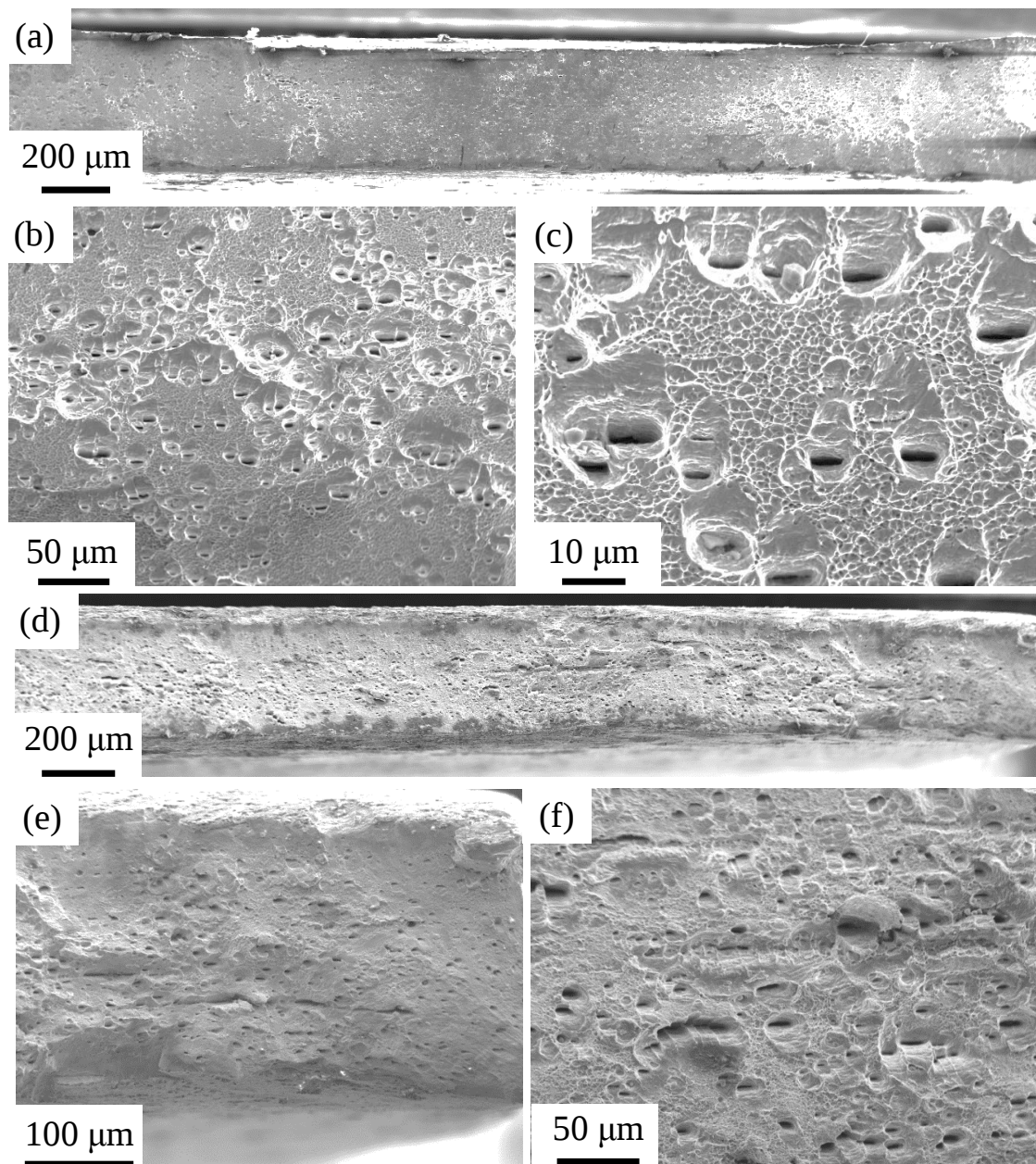


Figure 3.10 Fracture surfaces of the ultrafine-grained specimens with uncharged (a-c) and hydrogen-charged (d-f): (a) is the entire fracture surface of the hydrogen-uncharged specimen, (b) and (c) are the magnified images of (a). (d) is the entire fracture surface of the hydrogen-charged specimen, (e) and (f) are the magnified images of (d).

3.4. Discussion

3.4.1 Work hardening behaviors of the specimens with various grain sizes

Figure 3.11 shows true stress-strain curves and corresponding work hardening rate curves obtained from the nominal stress-strain curves of various grain-sized specimens. The true stress-strain curves were obtained, under an assumption of uniform deformation, from **Equation 3.1** and **Equation 3.2**, where s is the nominal stress, e is the nominal strain, σ is the true stress, and ε is the true strain.

$$\sigma = s(1+e) \quad (3.1)$$

$$\varepsilon = \ln(1+e) \quad (3.2)$$

The black and red lines indicate the uncharged and hydrogen-charged specimens, respectively. The work hardening was enhanced by grain refinement, regardless of hydrogen charging. The condition of plastic instability can be expressed by Considère criterion shown below [17],

$$\sigma \geq d\sigma / d\varepsilon \quad (3.3)$$

where σ is the true stress, ε is the true strain, and $d\sigma / d\varepsilon$ is the work hardening rate.

According to **Equation 3.3**, the intersection point of the work hardening rate curve and

true stress-strain curve corresponds to the plastic instability. When the work hardening rate becomes smaller than the corresponding true stress, necking takes place. In the present study, all the uncharged and hydrogen-charged specimens fractured after satisfying the plastic instability condition. However, the work hardening behaviors of the hydrogen-charged coarse-grained specimen exhibited a significant drop at the later stage of plastic deformation, leading to the earlier plastic instability. For the fine-grained specimen, a similar phenomenon was also observed, i.e., slightly earlier plastic instability in the hydrogen-charged specimen than that in the uncharged specimen. However, in the ultrafine-grained specimen, no significant difference was observed in the work hardening behaviors, indicating that hydrogen charging did not affect the work hardening behaviors even though the amount of diffusible hydrogen was larger in the ultrafine-grained specimen than that in the coarse grain-sized specimen (**Figure 3.3 (b)**).

Formation of the secondary cracks at the fracture surface in the hydrogen-charged coarse-grained specimen led to the reduction of cross-sectional area, resulted in the drop of apparent work hardening rate and then earlier plastic instability occurred. As a result, total elongation decreased in the hydrogen-charged coarse-grained specimen.

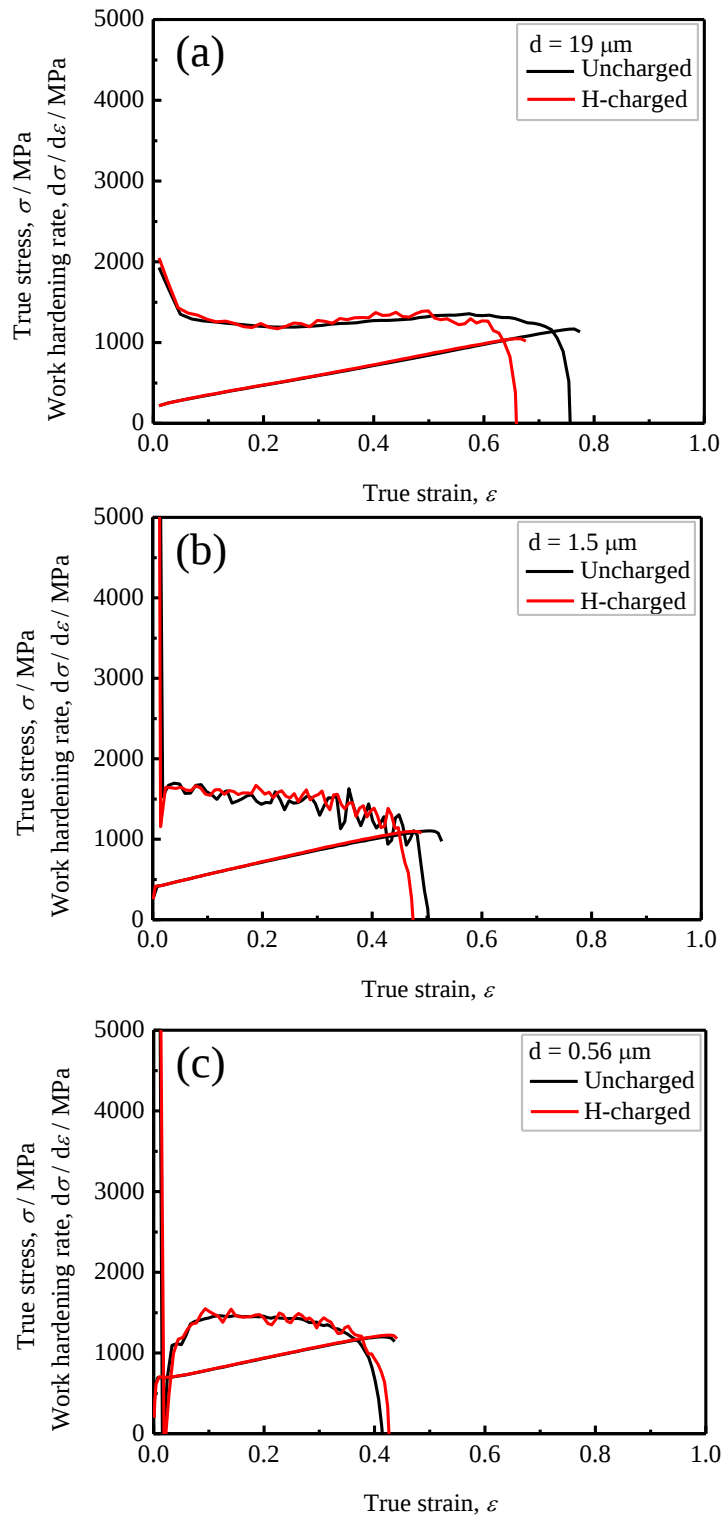


Figure 3.11 True stress-strain curves and work hardening rate curves of the 31Mn-3Al-3Si steel having different grain sizes with and without hydrogen charging: (a) coarse-grained specimens, (b) fine-grained specimens, and (c) ultrafine-grained specimens.

3.4.2 Diffusible hydrogen content at per unit grain boundary area

Possible trapping sites of hydrogen in the present specimens are inclusions, dislocations, twin boundaries, and grain boundaries. For inclusions, the hydrogen trapping energy is reported to be about 79 kJ / mol [18]. So *et al.* [19] reported that the hydrogen trapping energy of twin boundaries was around 62 kJ / mol. They are considered as relatively strong trapping sites for non-diffusible hydrogen. Hydrogen trapping energy of dislocations and grain boundaries is in the range of 20-46 kJ / mol [20], so that diffusible hydrogen is considered to be trapped by grain boundaries and dislocations.

Since the present specimens have fully recrystallized microstructures, the dislocation densities in the present specimens must be low. Thus, as a first step, we assume that grain boundaries trap all the diffusible hydrogen. Furthermore, diffusible hydrogen concentrated in the subsurface regions with the depth of 10 μm from the surface in the sheet specimens. Thus we assume as an extreme case that all diffusible hydrogen distributed uniformly at the grain boundaries existing in the 10 μm depth regions from the surfaces after the hydrogen charging process. The smaller the grain size, the larger the total grain boundary surface area per unit volume would be. Grain boundary area per unit volume, S_v , can be expressed as a function of mean interception

length of grains (mean grain size), d , as:

$$S_v = 2 / d \quad (3.4)$$

Therefore, the grain boundary area per unit volume in the specimens having the mean grain size excluding twin boundaries of 37 μm (coarse grains), 2.3 μm (fine grains) and 0.85 μm (ultrafine grains) are $5.4 \times 10^4 \text{ m}^2 / \text{m}^3$, $8.7 \times 10^5 \text{ m}^2 / \text{m}^3$ and $2.4 \times 10^6 \text{ m}^2 / \text{m}^3$, respectively. Consequently, with decreasing the grain size the trapping sites of diffusible hydrogen increases, which coincides with the present result that the largest amount of diffusible hydrogen was introduced in the ultrafine-grained specimen (**Figure 3.3**).

Diffusible hydrogen contents in the surface regions with thickness of 10 μm (X_H^{all}) were calculated by the values shown in **Table 3.1**: 98.8 wt ppm in the coarse-grained specimen, 128.9 wt ppm in the fine-grained specimen, and 211 wt ppm in the ultrafine-grained specimen, respectively. Corresponding local diffusible hydrogen contents in the unit surface area of grain boundary (x_H^{GB}) were $1.4 \times 10^{-2} \text{ g} / \text{m}^2$, $1.2 \times 10^{-3} \text{ g} / \text{m}^2$ and $7.0 \times 10^{-4} \text{ g} / \text{m}^2$, respectively, which were obtained from following formula:

$$x_H^{GB} = w_H / S_v \quad (3.5)$$

where w_H is the weight content of hydrogen per unit volume of the specimen. That is,

the local hydrogen content at the unit surface area of grain boundary decreased with decreasing the mean grain size. All these values are summarized in **Table 3.3**.

Table 3.3 Summary of the grain size (d), grain boundary area per unit volume (S_v), content of diffusible hydrogen in the surface regions with thickness of 10 μm (X_H^{all}), and hydrogen content per unit grain boundary area (x_H^{GB}) calculated under an assumption that all hydrogen locates at grain boundaries.

Mgrain size, $d / \mu\text{m}$	Grain boundary area per unit volume, $S_v / \text{m}^2 / \text{m}^3$	Diffusible hydrogen content at the subsurface with 10 μm thick, $X_H^{all} / \text{wt ppm}$	Diffusible hydrogen content per unit grain boundary area, $x_H^{GB} / \text{g} / \text{m}^2$
37	5.4×10^4	98.8	1.4×10^{-2}
2.3	8.7×10^5	128.9	1.2×10^{-3}
0.85	2.4×10^6	211	7.0×10^{-4}

The assumption used in **Table 3.3** that all diffusible hydrogen is trapped at grain boundaries is the most extreme condition and not realistic. A certain amount of hydrogen must exist in the austenite matrix (grain interior) or weak trapping sites besides grain boundaries. In fact, it is known that the solubility of hydrogen in austenitic steel is relatively high. According to a previous literature [21], for example, the solubility of hydrogen in a Type 304L austenitic stainless steel was 72 wt ppm in 69 MPa hydrogen gas at 197 °C. Although it is difficult to experimentally distinguish the amount of hydrogen existing at the grain boundaries from that in the matrix, we can

simply calculate the partition of hydrogen into grain boundaries and matrix, by the use of the values shown in **Table 3.3**. That is, we have measured the total amount of diffusible hydrogen by TDS, and have calculated the hydrogen content per unit grain boundary area under an assumption that all diffusible hydrogen locates at grain boundaries, for three kinds of specimens with different grain sizes. The relationship between the hydrogen content in the matrix (X_H^M) and the hydrogen content per unit grain boundary area (x_H^{GB}) is shown in **Figure 3.12**. It was found that three lines intersect to each other at nearly the same point indicated as “A” in the figure, i.e., the coarse-grain’s line meets with those of the fine-grained and ultrafine-grained specimens at $X_H^M = 96.8$ wt ppm and 96.2 wt ppm, respectively, and the line of fine-grained specimen intersects with that of the ultrafine-grained specimen at 80.8 wt ppm. That is, the figure indicates that the amount of hydrogen at grain boundaries in the fine-grained or ultrafine-grained specimens can be larger than that in the coarse-grained specimen only when X_H^M is larger than 96.8 wt ppm. However, 96.8 wt ppm is 98 % of the total diffusible hydrogen included in the coarse-grained specimen, which seems unrealistic. It can be, therefore, concluded that the amount of hydrogen at grain boundaries in the ultrafine-grained specimen is much lower than that in the coarse-grained specimen, even

if some amount of hydrogen exists at grain interior, which would be the main reason why hydrogen did not influence the ductility of the ultrafine-grained specimen.

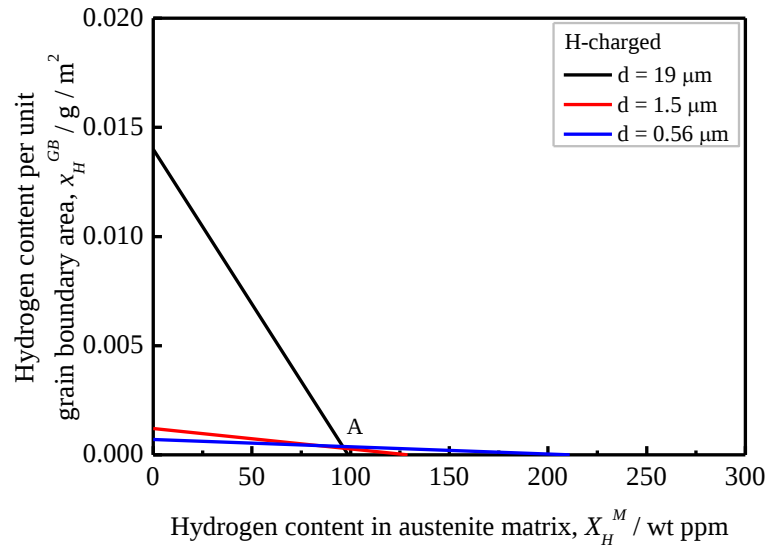


Figure 3.12 Relationship between the hydrogen content in austenite matrix (grain interior) and the hydrogen content per unit grain boundary area, which is obtained from the values in **Table 3.3**. The point A around which the hydrogen content per unit grain boundary area of the coarse-grained specimens becomes smaller than that of the fine-grained and ultrafine-grained specimens corresponds to around 96.8 wt ppm of the hydrogen content in the matrix.

3.4.3 Stress concentration at grain boundaries

Besides the static condition of hydrogen existence, the deformation of materials also plays an important role on hydrogen accumulation.

Grain boundary is a main stress concentration site in polycrystalline material. It is known that the diffusible hydrogen atoms tend to accumulate at high stress concentration sites [22]. The higher the stress concentration, the more diffusible hydrogen accumulates. During deformation, mobile dislocations can pile-up against

the grain boundaries and thus give rise to stress concentration. The stress concentration increases with increasing the number of dislocations pile-up at grain boundaries. The amount of dislocations pile-up at grain boundaries decreases with decreasing the grain size. That is to say, in the present study, the amount of dislocations pile-up at grain boundaries was larger in the coarse-grained specimen than that in the ultrafine-grained specimen. So that the stress concentration at grain boundaries was larger in the coarse-grained specimen and resulted in higher concentration of diffusible hydrogen accumulates at grain boundaries. In addition, the pile-up length of slip dislocations decreases with decreasing the grain size. Therefore we suppose that in the present study, the secondary cracks observed on the fracture surfaces in the hydrogen-charged coarse-grained specimen (**Figure 3.8 (d)**) is probably due to the higher concentration of hydrogen at the grain boundaries than that in the hydrogen-charged ultrafine-grained specimen.

Accordingly, we conclude that the grain refinement suppressed the hydrogen content per unit grain boundary area during hydrogen charging process, and also suppressed the hydrogen accumulation at grain boundaries by stress concentration during the tensile test. The above two effects resulted in the less sensitivity to the hydrogen embrittlement by decreasing the grain size in the 31Mn-3Al-3Si steel.

3.5 Conclusions

In the present study, the 31Mn-3Al-3Si steel having different mean grain sizes of 19 μm , 1.5 μm , and 0.56 μm were used to investigate the effect of grain size on the hydrogen embrittlement behaviors, using a slow strain rate tensile test. The results obtained in this chapter are summarized below:

1. In the result of tensile tests, hydrogen charging had no influence on the yield strength and ultimate tensile strength but induced a certain decrease in the total elongation. The total elongation kept almost the same value in the ultrafine-grained specimens regardless of hydrogen charging, whereas a significant drop of the total elongation was observed in the coarse-grained specimen. All the tested specimens fractured after satisfying the plastic instability condition. However, a significant drop of work hardening rate was observed at later stage of deformation in the hydrogen-charged coarse-grained specimen, whereas no significant difference was observed in the work hardening behaviors in the ultrafine-grained specimens. It indicated that mechanical properties became less susceptibility to hydrogen with decreasing the grain size.
2. All the fracture surfaces showed ductile fracture with dimple patterns. Some large secondary cracks were observed in the hydrogen-charged coarse-grained specimen,

whereas some relatively small cracks were observed in the fine-grained specimen and almost no secondary crack were observed in the ultrafine-grained specimen. The large secondary cracks were considered to be the reason for the apparent earlier plastic instability in the hydrogen-charged coarser-grained specimen.

3. The result of TDS measurement indicated that the diffusible hydrogen content increased with decreasing the mean grain size and the diffusible hydrogen concentrated within 10 μm thick surface layers. However, the diffusible hydrogen content per unit area of grain boundary increased with increasing the mean grain size. Moreover, the degree of local hydrogen accumulation at grain boundaries by stress concentration during plastic deformation was considered to be larger in the coarse-grained specimen than that in the ultrafine-grained specimen. The above mentioned two factors could be the reason for the suppression of hydrogen embrittlement by grain refinement in the 31Mn-3Al-3Si steel.

3.6 References

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Chapter 4 Hydrogen embrittlement behaviors of different grain-sized 22Mn-0.6C austenitic steel

4.1 Introduction

As introduced in **Chapter 1**, Mn-C austenitic steels, in particular Fe-18Mn-0.6C (wt. %) and Fe-22Mn-0.6C (wt. %), are the most typical and common high-manganese austenitic steels showing very high strength and large ductility as well as large strain hardening rate. Recently, Koyama et al. [1-4] have done several works on the hydrogen embrittlement behaviors of Mn-C high-manganese austenitic steels. They investigated hydrogen embrittlement properties of an 18Mn-0.6C austenitic steel by a tensile test under hydrogen charging [1]. According to their results, the total elongation deteriorated significantly by hydrogen charging (**Figure 4.1** (a)), and intergranular fracture occurred in the vicinity of the sample surface of the hydrogen-charged specimen (**Figure 4.2** (b)). They revealed that deformation twins assisted hydrogen-related intergranular crack initiation and propagation in the 18Mn-1.15C austenitic steel [2]. The effect of Al in the Mn-C austenitic steels on hydrogen embrittlement behaviors was also investigated [5-7]. The results showed that hydrogen embrittlement was suppressed by addition of Al in the Mn-C austenitic

steels.

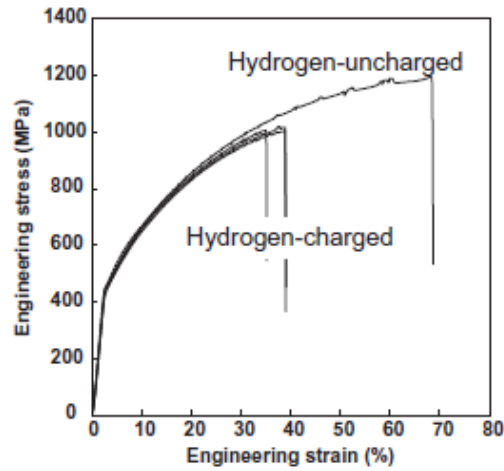


Figure 4.1 Nominal stress-strain curves of the uncharged and hydrogen-charged 18Mn-0.6C steel reported by Koyama et al. [1].

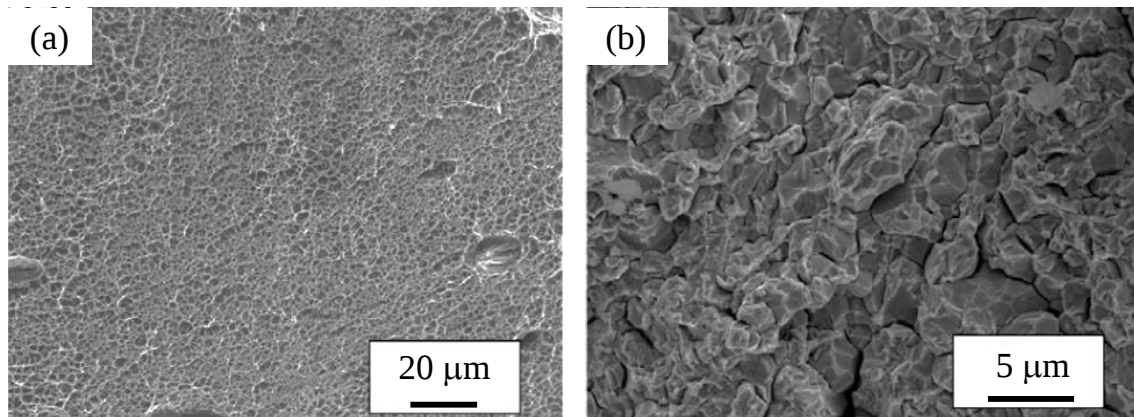


Figure 4.2 Fracture surfaces of the 18Mn-0.6C austenitic steel with and without hydrogen charging reported by Koyama et al. [1]: (a) uncharged specimen, (b) hydrogen-charged specimen.

In general, susceptibility to hydrogen embrittlement increases with increasing the strength [8]. Grain refinement is a very effective way to strengthen materials.

Previous studies revealed that grain refinement enhanced the resistance to hydrogen

embrittlement [9, 10]. Although the grain sizes were still in a range of relatively large sizes in the previous studies mentioned above, we expect that the resistance to hydrogen embrittlement would be enhanced much more by refining the grain size from several tens micro-meters to nanometer scale in high-manganese austenitic steels.

The aim of the present chapter is to investigate the relationship between the grain sizes ranging from coarse several tens micro-meter scale to ultrafine submicro-meter scale and the hydrogen embrittlement behaviors in the 22Mn-0.6C austenitic steel, which has different chemical composition and mechanical properties from the 31Mn-3Al-3Si steel studied in **Chapter 3**.

4.2 Experimental procedure

4.2.1 Materials

A 22Mn-0.6C (wt. %) austenitic steel was used in this study. The chemical composition of the alloy was listed in **Table 2.2** of **Chapter 2**.

4.2.2 Hydrogen pre-charging

Hydrogen was pre-charged by the cathodically electro-charging method. Hydrogen was introduced into the tensile test specimens in a 3 % NaCl + 3 g / L NH_4SCN aqueous solution with a current density of $100 \text{ A} / \text{m}^2$ for 172.8 ks (48 hr) at room temperature. The details were described in the section **3.2.2** in **Chapter 3**.

4.2.3 Hydrogen content measurement

The amount of hydrogen content was measured by thermal desorption spectroscopy (TDS). The gauge part (10 mm in length, 5 mm in width) was cut out from the tensile test specimen immediately after the hydrogen charging. Then, the TDS measurements were started exactly 1.8 ks after finishing the hydrogen charging, in

order to keep the amount of hydrogen escaped from the specimen surface the same in every hydrogen-charged specimen. The specimen was heated from room temperature to 800 °C at a heating rate of 100 °C / hr, and the desorbed gas was analyzed at 5 min intervals using argon as a carrier gas. Argon gas mixed with hydrogen gas was used for the calibration.

4.2.4 Diffusible hydrogen distribution

In order to estimate the distribution of hydrogen inside the specimen after the hydrogen charging, the surface layer of the hydrogen-charged specimens was removed by mechanical polishing by thickness of 5 µm or 10 µm from both sides of the specimen immediately after the hydrogen charging completed, and then TDS measurement was carried out.

4.2.5 Slow strain rate tensile test

The tensile test specimens with a gauge length of 10 mm, a width of 5 mm, and a thickness of 0.6 mm were fabricated from the 1 mm thick cold-rolled and subsequently annealed sheets. The detailed dimension of the tensile test specimen was illustrated in

Figure 3.3. Hydrogen embrittlement behaviors were evaluated by the uniaxial tensile test using a tensile machine (Shimadzu, AG-X plus, 100 kN) at a crosshead speed of 5×10^{-3} mm / min, corresponding to an initial strain rate of 8.3×10^{-6} / s. In order to keep the same condition of the tensile test for every hydrogen-charged specimen, the tensile test was started exactly 1.8 ks after the hydrogen charging process was completed. Two tensile tests were carried out for each uncharged and hydrogen-charged specimen. An extensometer (Shimadzu, SG10-100) was attached to the gauge part of the specimen to measure the tensile strain precisely in the tensile test. The strain data were collected by the extensometer until the displacement reached 0.2 mm. Beyond the 0.2 mm range, the displacement was calculated by the stroke of the cross-head.

4.2.6 Fracture surface observation

The fracture surfaces of the tensile-tested specimens were examined by a field emission type scanning electron microscope (FE-SEM, JEOL JSM-7800F) with a back scattering electron (BSE) detector, operated at an acceleration voltage of 15 kV.

4.2.7 Fracture toughness

Three-point bending test was carried out to evaluate the fracture toughness of the uncharged and hydrogen-charged specimens. The strain rate used was $8.3 \times 10^{-6} / \text{s}$, which was the same as that in the slow strain rate tensile test. The test was also started exactly 1.8 ks after the hydrogen charging was completed. The dimension of the three-point bending test specimen is shown in **Figure 4.3**. The specimen length (L) is 20 mm, width (W) is 3 mm, thickness (B) is 1 mm, and the distance of supporting pins (S) is 12 mm. A notch with a length of 1.5 mm and a radius of 0.2 mm was introduced by a discharge wire cutting machine.

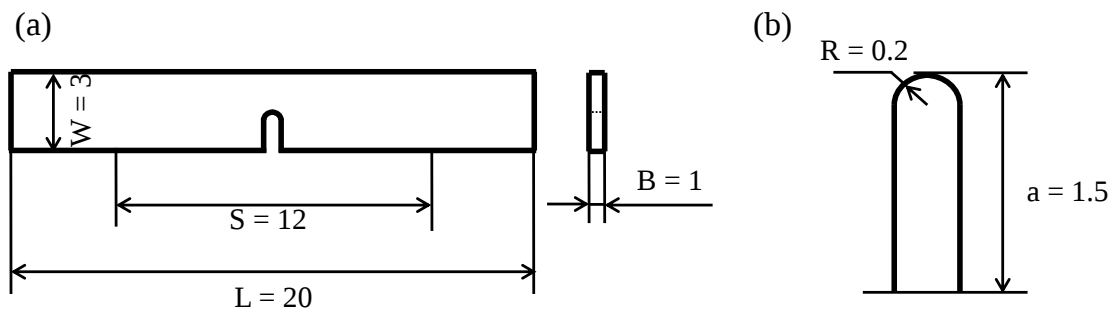


Figure 4.3 Schematic illustration of the three-point bending test specimen (a), and detailed dimensions of the notch (b). B: thickness, W: width, S: distance of supporting pins, L: length, a: notch length, R: notch root radius.

4.3 Results

4.3.1 Microstructure characterization

As was shown in **Figure 2.13**, the as-received hot-forged specimen in the 22Mn-0.6C steel had the mean grain size of 21 μm counting in annealing twins or 44 μm excluding annealing twins. Through the four-step cold rolling and subsequent annealing process, the specimens with two kinds of grain sizes were obtained. The mean grain sizes were 1.5 μm / 2.3 μm , and 0.58 μm / 0.69 μm including / excluding annealing twins. The detailed microstructures are omitted here, since they were already shown in **Figure 2.13**. In order to investigate the effect of grain size on hydrogen embrittlement behaviors in the 22Mn-0.6C austenitic steel, the specimens with the grain size of 0.58 μm and 21 μm (counting in twin boundaries) were chosen in the present study. They are termed as the ultrafine-grained specimen and the coarse-grained specimen, respectively.

4.3.2 Diffusible hydrogen content

The hydrogen desorption rate curves of the uncharged and hydrogen-charged specimens obtained by the TDS measurement are shown in **Figure 4.4**. The hydrogen

released below 200 °C was defined as diffusible hydrogen in the present study. In the uncharged specimens (**Figure 4.4 (a)**), the peak of diffusible hydrogen in the lower temperature range was not observed. On the other hand, obvious peaks of diffusible hydrogen were observed in the specimens after hydrogen charging in both the coarse-grained specimen and the ultrafine-grained specimen, as shown in **Figure 4.4 (b)**. The integrated area under the curve gives the amount of diffusible hydrogen released from the specimen during heating. The diffusible hydrogen contents were 0.98 wt ppm and 1.07 wt ppm in the coarse-grained and ultrafine-grained specimens, respectively. There was almost no change in the diffusible hydrogen content between the hydrogen-charged ultrafine-grained specimen and the hydrogen-charged coarse-grained specimen, which is different from the 31Mn-3Al-3Si steel studied in

Chapter 3.

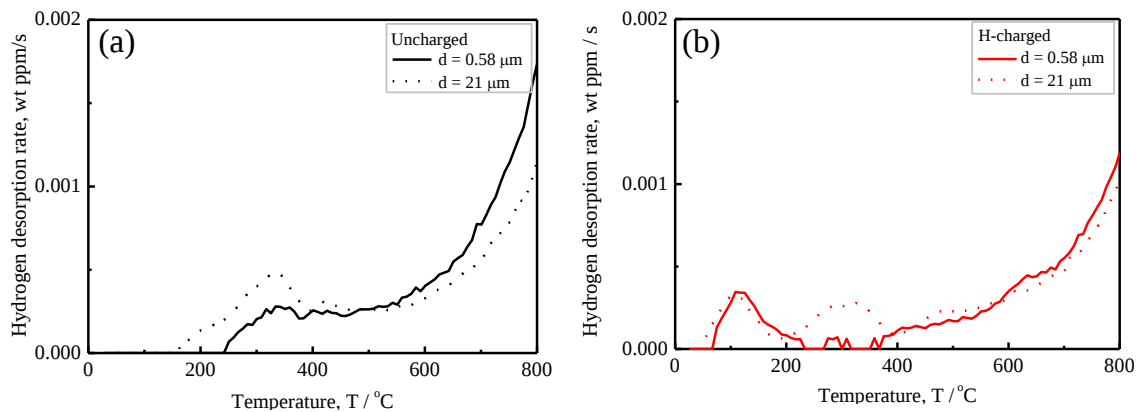


Figure 4.4 Hydrogen desorption rate curves of the coarse-grained and ultrafine-grained specimens of the 22Mn-0.6C steel obtained from the TDS measurement: (a) the uncharged specimens, and (b) the hydrogen-charged specimens.

4.3.3 Hydrogen diffusion distance

Figure 4.5 shows hydrogen desorption rate curves of the hydrogen-charged specimens after surface layers were removed by thickness of 5 μm or 10 μm from both sides of the specimens. The curves of the hydrogen-charged specimens without removing the surface layers are also indicated in **Figure 4.5**. In both the coarse-grained specimen and the ultrafine-grained specimen, the peaks of diffusible hydrogen content became small after removing 5 μm surface layers (as indicated by red lines), compared with the unremoved one (indicated by black lines). Furthermore, almost no hydrogen was detected after removing 10 μm surface layers in the coarse-grained specimen, whereas some content of diffusible hydrogen was still left in the ultrafine-grained specimen (as indicated by pink lines). The diffusible hydrogen content in the remnant of the specimens after removing various thicknesses of surface layers is summarized in **Table 4.1**.

Figure 4.6 shows diffusible hydrogen concentration profiles obtained from **Table 4.1**. The bar indicates the hydrogen content in each 5 μm thick layer from the surface to inside. The result suggests that diffusible hydrogen concentrated within the 10 μm thick surface layer in the coarse-grained specimen. In the case of the ultrafine-grained specimen, hydrogen diffused deeper than in the coarse-grained specimen. However,

the depth is probably less than several tens micro-meters even in the ultrafine-grained specimen.

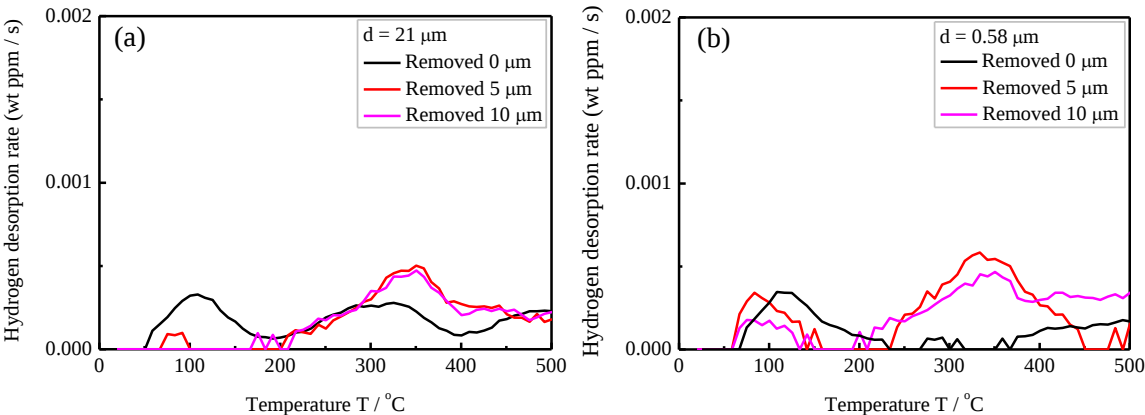


Figure 4.5 Hydrogen desorption rate curves of the hydrogen-charged specimens with different grain sizes after removing the surface layer by thickness of 0 μm , 5 μm and 10 μm : (a) the coarse-grained specimens, and (b) the ultrafine-grained specimens.

Table 4.1 Summary of diffusible hydrogen content in the specimens after removing the surface layers by thickness of 0 μm , 5 μm or 10 μm , respectively, in the 22Mn-0.6C steel.

Mean grain size, $d / \mu\text{m}$	21			0.58		
Thickness of removed surface layer, $t / \mu\text{m}$	0	5	10	0	5	10
Diffusible hydrogen content in the remainder of the specimen, wt ppm	0.98	0.08	0.06	1.07	0.7	0.38

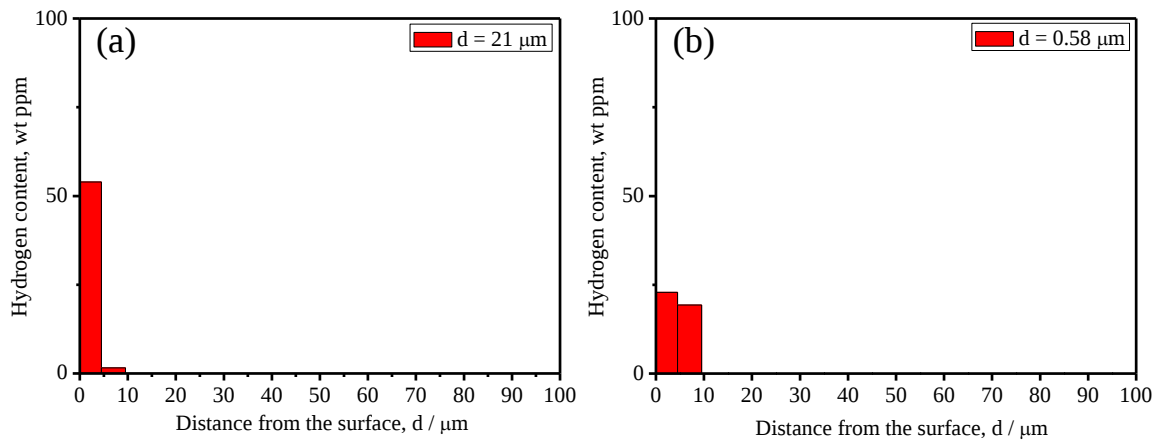


Figure 4.6 Diffusible hydrogen content profile as a function of the distance from the surface: (a) the coarse-grained specimen, and (b) the ultrafine-grained specimen.

4.3.4 Mechanical properties

Figure 4.7 shows nominal stress-strain curves of the uncharged and hydrogen-charged specimens of the 22Mn-0.6C steel with different grain sizes. The strength increased significantly with decreasing the grain size from 21 μm to 0.58 μm. Serrations, which are common in high-manganese austenitic steels with carbon, were recognized in the stress-strain curves. This would be related to the dynamic interaction between gliding dislocations and mobile solute atoms, namely dynamic strain aging [11]. Compared with the uncharged specimens, the hydrogen-charged specimens having corresponding grain sizes were fractured at lower strains and lower stresses. The mechanical properties obtained from the tensile tests are summarized in **Table 4.2**. It was found from **Table 4.2** that the hydrogen charging led to the decrease of ultimate

tensile stress and total elongation, whereas yield strength was not affected in both the coarse-grained and the ultrafine-grained specimens.

Figure 4.8 shows true stress-strain curves as well as work hardening rate curves of the uncharged and hydrogen-charged specimens with coarse grains and ultrafine grains. The intersection of the true stress-strain curve and the work hardening rate curve corresponds to the initiation of necking, called plastic instability. Considère's criterion for plastic instability is expressed as below [12]:

$$\sigma \geq d\sigma / d\varepsilon \quad (4.1)$$

where σ is the true stress, ε is the true strain, and $d\sigma / d\varepsilon$ is the work hardening rate. When the work hardening rate becomes smaller than the true flow stress, necking takes place. It was found from **Figure 4.8** that the uncharged specimens fractured after plastic instability (necking), whereas the hydrogen-charged specimens fractured before plastic instability (necking) occurred.

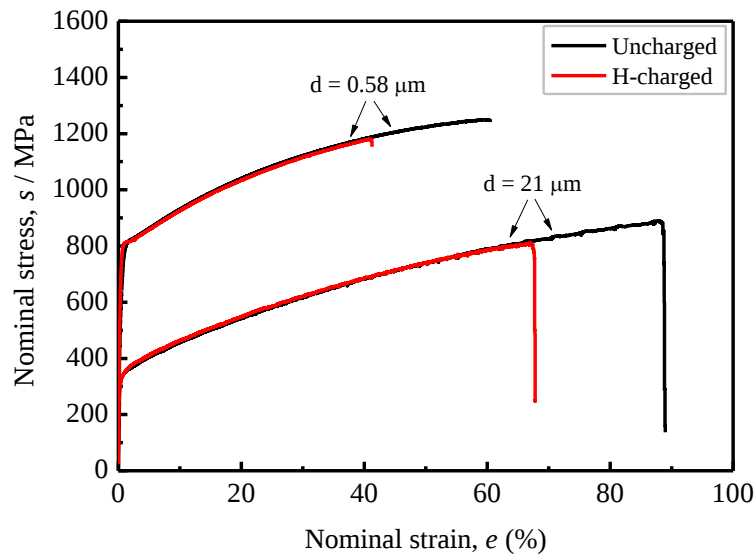


Figure 4.7 Nominal stress-strain curves of the uncharged and hydrogen-charged specimens of the 22Mn-0.6C steel with different grain sizes.

Table 4.2 Mechanical properties obtained from the tensile tests of the uncharged and hydrogen-charged specimens having different grain sizes: yield strength (σ_y), ultimate tensile strength (σ_{UTS}), and total elongation (e_{total}).

Mean grain size, $d / \mu\text{m}$ (include / exclude annealing twins)	Condition	Yield strength, σ_y / MPa	Ultimate tensile strength, $\sigma_{UTS} / \text{MPa}$	Total elongation, $e_{total} / \%$
21 / 44	Uncharged	371	889	89
	Hydrogen-charged	377	811	67.8
0.58 / 0.69	Uncharged	823	1249	60.4
	Hydrogen-charged	817	1179	41.2

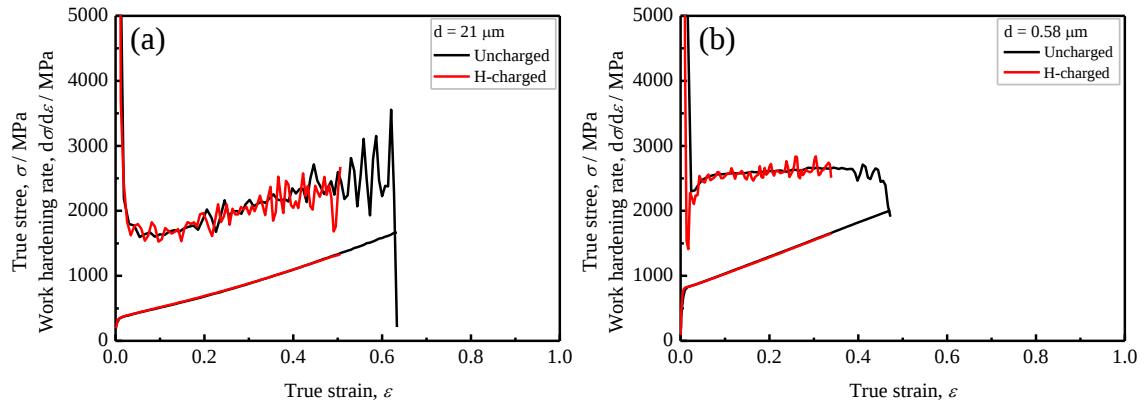


Figure 4.8 True stress-strain curves and work hardening rate curves of the uncharged and hydrogen-charged specimens obtained from the nominal stress-strain curves: (a) the coarse-grained specimens, and (b) the fine-grained specimens.

4.3.5 Fracture surface observation

Figure 4.9 shows SEM images of fracture surfaces of the uncharged and hydrogen-charged specimens having different grain sizes after the slow strain rate tensile test. The relatively flat fracture surfaces covered by a large number of dimples were observed in the uncharged specimens (**Figure 4.9** (a) and (c)). On the other hand, the fracture surfaces of the hydrogen-charged specimens comprised the regions other than dimples as indicated by black dotted squares (**Figure 4.9** (b) and (d)).

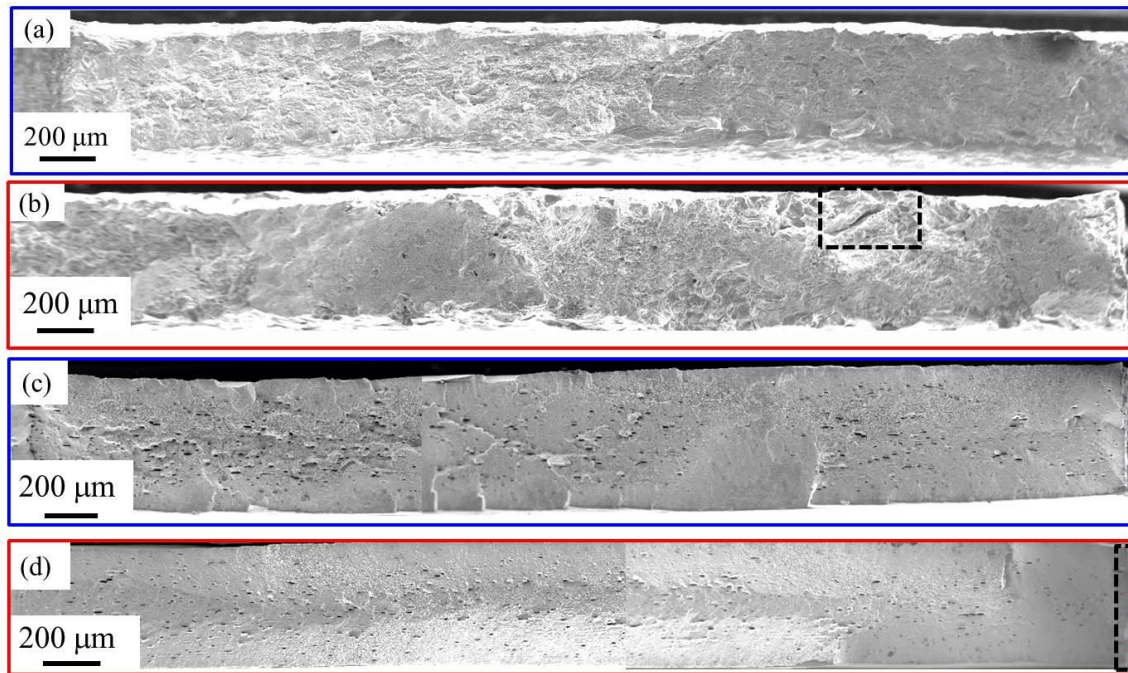


Figure 4.9 SEM images of fracture surfaces of the uncharged and hydrogen-charged 22Mn-0.6C steel with different grain sizes: (a) the uncharged coarse-grained specimen, (b) the hydrogen-charged coarse-grained specimen, (c) the uncharged ultrafine-grained specimen, and (d) the hydrogen-charged ultrafine-grained specimen.

The fracture surfaces of the uncharged coarse-grained specimen consisted of dimples, indicating that ductile fracture occurred (**Figure 4.10** (a)). Most of the hydrogen-charged fracture surfaces were covered by dimples (**Figure 4.10** (b)), which were similar to those of the uncharged one. However, brittle fracture surfaces were partially observed near the surface of the specimen as shown in **Figure 4.10** (c), which is the magnified image of the region highlighted by the black dotted square in **Figure 4.9** (b). Furthermore, the brittle fracture surfaces consisted of two types of surfaces as

shown in **Figure 4.9** (d): one was a relatively smooth surface (surrounded by black lines) with the shape of grain and the other was surface including parallel traces (surrounded by white lines). Concerning the latter one, similar fracture surfaces were also reported in a 23Mn-0.6C steel tested in hydrogen gas atmosphere [13]. Secondary cracks along grain boundaries accompanying with many parallel traces were also observed (**Figure 4.10** (e)). The parallel traces might correspond to slip lines. However, the detail has not been clarified yet. The depth position of the brittle fracture part was ranging from 50 μm to 150 μm from the surface.

The dimple size in the hydrogen-charged coarse-grained specimen was approximately 3 μm . Compared with the coarse-grained specimen, the size of the dimples was 0.8 μm in both the uncharged and hydrogen-charged ultrafine-grained specimen (**Figure 4.11** (a, b)), which was very fine. As shown in **Figure 4.11** (c), (d), the region at the edge of the specimen indicated by black dotted square in **Figure 4.9** (d) composed of brittle fracture surfaces. The traces similar to **Figure 4.10** (d) were also observed as shown in **Figure 4.11** (d). Depth of the brittle fracture regions were around 10 μm from the specimen surface.

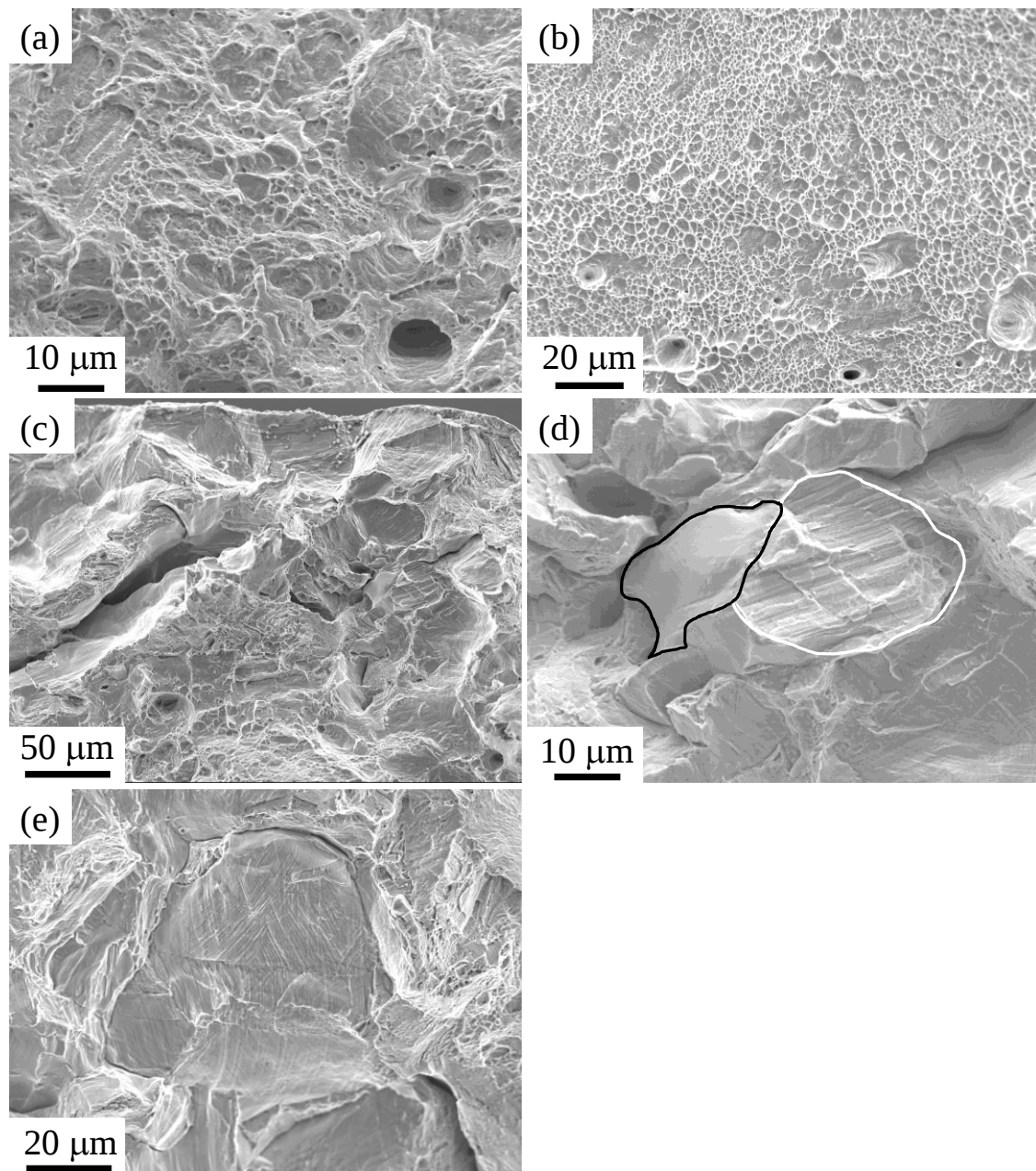


Figure 4.10 SEM images of fracture surfaces of the coarse-grained specimens: (a) uncharged, (b-e) hydrogen-charged.

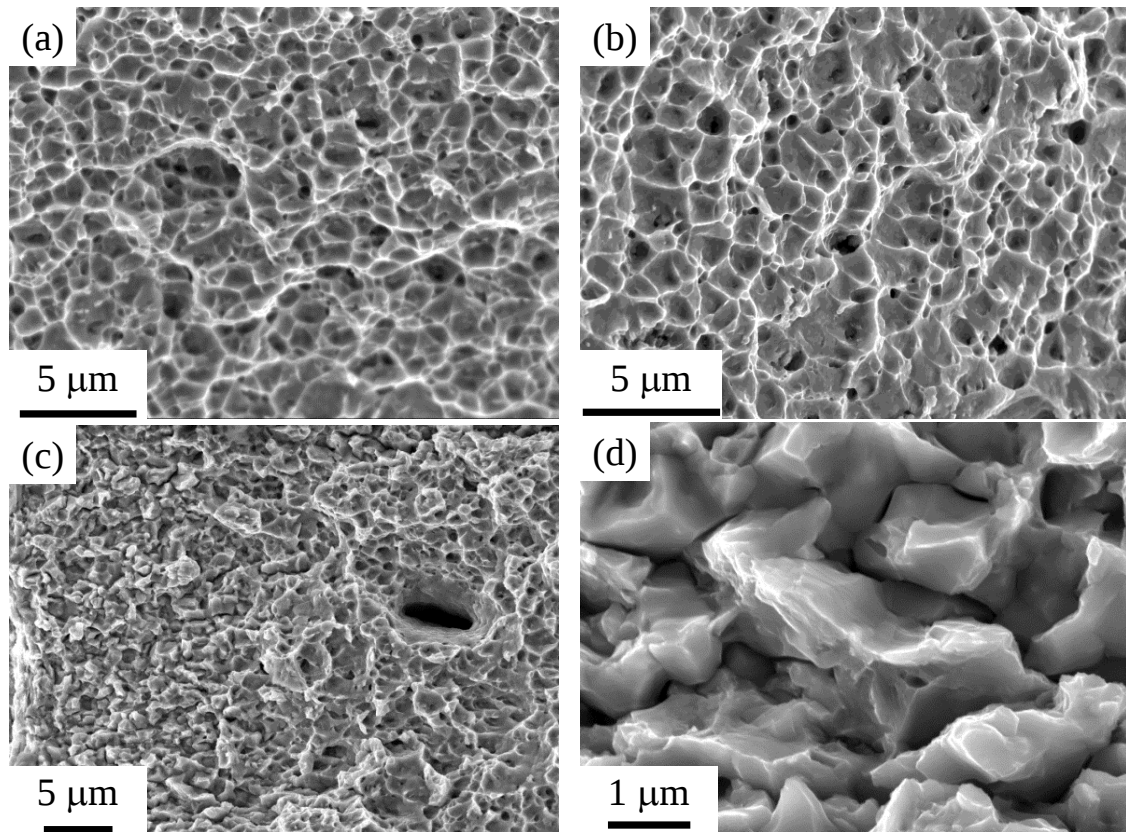


Figure 4.11 SEM images of fracture surfaces of the ultrafine-grained specimens: (a) uncharged, (b-d) hydrogen-charged.

4.3.6 Fracture toughness

Figure 4.12 shows load-displacement curves obtained from the three-point bending test of the coarse-grained specimens and ultrafine-grained specimens with and without hydrogen charging. Black lines and red lines indicate the uncharged specimens and the hydrogen-charged specimens, respectively. Compared with the coarse-grained specimens, the ultrafine-grained specimens exhibited smaller plastic deformation. Note that all the specimens did not fracture after the three-point bending

tests. This indicates that the 22Mn-0.6C steel is not a brittle material but quite ductile.

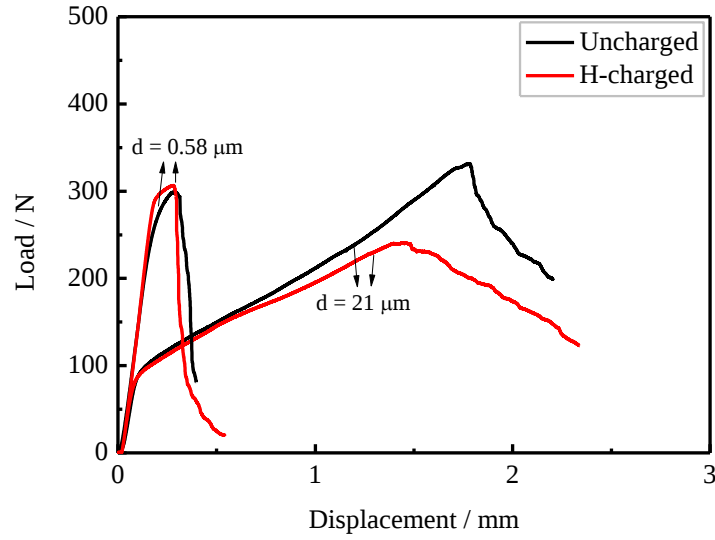


Figure 4.12 Load-displacement curves of the 22Mn-0.6C steel obtained from the three-point bending test.

The stress intensity factor, K_Q , is calculated by the equation shown below [15]:

$$K_Q = \frac{P_Q f\left(\frac{a}{W}\right)}{B\sqrt{W}} \quad (4.2)$$

$$f\left(\frac{a}{W}\right) = \frac{\frac{3S}{W} \sqrt{\frac{a}{W}}}{2\left(1 + 2\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)^{3/2}} \left[1.99 - \frac{a}{W}\left(1 - \frac{a}{W}\right)\right. \\ \left.\left\{2.15 - 3.93\frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right\}\right] \quad (4.3)$$

where, P_Q is a load at fracture initiation, a is a notch length, W is a specimen width, B is a specimen thickness, and S is a specimen span. When a specimen exhibits plastic

deformation to some extent, the P_Q is defined as the load at which the line having a slope of 95 % elastic modulus intersects the load-displacement curve, as shown in **Figure 4.13**. When the following conditions are satisfied, the obtained K_Q value can be regarded as fracture toughness.

$$0.45 \leq \frac{a}{W} \leq 0.55 \quad (4.4)$$

$$B, a \geq 2.5 \left(\frac{K_Q}{\sigma_y} \right)^2 \quad (4.5)$$

$$P_{max} \leq 1.10P_Q \quad (4.6)$$

where σ_y is the yield strength of the material, and P_{max} is the maximum load in a load-displacement curve.

In the present case, **Equation 4.4** is satisfied, but **Equation 4.5** and **Equation 4.6** are not satisfied because of large plastic deformation of the 22Mn-0.6C steel. Accordingly, strict fracture toughness cannot be obtained from the present three-point bending test. Then, assuming that P_{max} corresponds to the load of fracture initiation P_Q , the apparent fracture toughness, K_A , was calculated using the value of P_{max} in the load-displacement curves shown in **Figure 4.12**. The obtained values are summarized in **Table 4.3**. It was found that the apparent fracture toughness decreased significantly by hydrogen-charging in the coarse-grained specimens. In the ultrafine-grained

specimens, however, the apparent fracture toughness did not change by hydrogen charging.

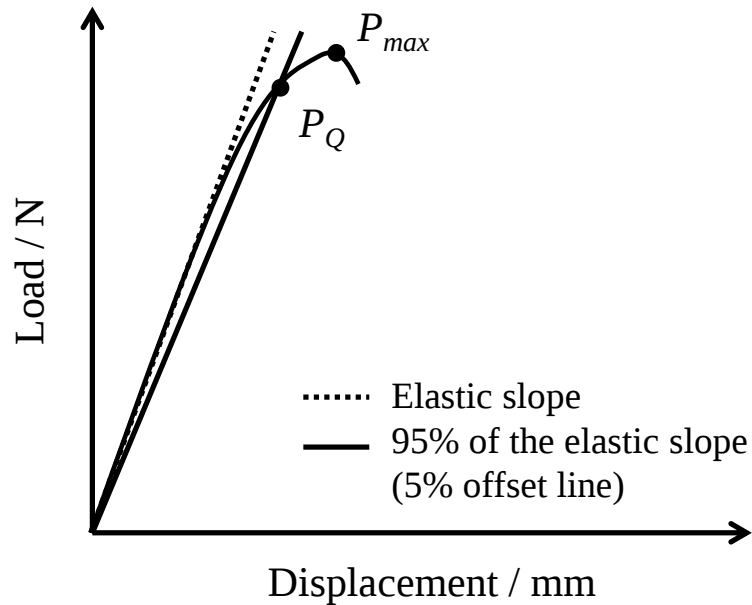


Figure 4.13 Schematic illustration for determining P_Q value on a load-displacement curve for strictly obtaining the fracture toughness K_Q .

Table 4.3 Summary of the yield strength, maximum load, and apparent fracture toughness in the 22Mn-0.6C steel having different grain sizes with and without hydrogen charging.

Mean grain size, $d / \mu\text{m}$	Condition	Yield strength, σ_y / MPa	Maximum load, P_{max} / N	Apparent fracture toughness, $K_A / \text{MPa m}^{1/2}$
21	Uncharged	371	331.5	63.2
	Hydrogen-charged	377	240.6	45.86
0.58	Uncharged	823	298.9	57
	Hydrogen-charged	817	306.4	58.4

4.4 Discussion

4.4.1 Hydrogen embrittlement susceptibility of 22Mn-0.6C steel with different grain sizes

In the slow strain rate tensile tests, the ultimate tensile strength and total elongation decreased significantly by hydrogen charging in both the coarse-grained specimen and the ultrafine-grained specimen. However, the fracture surfaces of the hydrogen-charged specimens showed some differences. Except the shown brittle fracture surfaces in **Figure 4.9 (b)** in the hydrogen-charged coarse-grained specimen, some other brittle fracture surfaces were also observed near the specimen surface. In the hydrogen-charged coarse-grained specimen, brittle fracture surfaces were also observed at the opposite edge to the brittle fracture surfaces shown in black dotted square in **Figure 4.9 (d)**. The fractions of brittle fracture surfaces in the coarse-grained specimen and the ultrafine-grained specimen were 8.6 % and 0.6 %, respectively, indicating that the fraction of the brittle fracture surfaces became clearly small with decreasing the grain size. Furthermore, the reduction of apparent fracture toughness (K_A) after hydrogen charging obtained by the three-point bending test was suppressed in the ultrafine-grained specimen. The above results indicate that hydrogen embrittlement is suppressed by decreasing the grain size in the 22Mn-0.6C steel.

4.4.2 Diffusible hydrogen content at per unit grain boundary area

In the hydrogen desorption rate curves shown in **Figure 4.4**, all the hydrogen-charged specimens exhibited only one peak around 110 °C, which corresponded to the hydrogen released from either dislocations or grain boundaries [16]. Since the specimens have fully recrystallized microstructures with coarse grains and ultrafine grains, the dislocation density must not be different too much. The difference in the grain size results in a great difference in the grain boundary surface area, which would be the main trapping site for diffusible hydrogen. That is to say, the increasing grain boundary area with decreasing the grain size is expected to cause the increase of diffusible hydrogen content, like the changes of hydrogen content in the 31Mn-3Al-3Si steel shown in **Chapter 3**. However, the diffusible hydrogen contents were not affected by the grain size in the 22Mn-0.6C steel.

Furthermore, diffusible hydrogen concentrated in the subsurface regions with the depth of 10 µm from the surface in the sheet specimens. Thus we assume as an extreme case that all diffusible hydrogen distributed uniformly at the grain boundaries existing within the 10 µm depth regions from the surface after the hydrogen charging process. Grain boundary area per unit volume, S_v , can be expressed as a function of the mean interception length of grains (mean grain size), d , as :

$$S_v = 2 / d \quad (4.7)$$

According to **Equation 4.7**, the grain boundary area per unit volume in the specimens having the mean grain size of 44 μm (coarse grains, without counting in twin boundaries), and 0.69 μm (ultrafine grains) are $4.5 \times 10^4 \text{ m}^2 / \text{m}^3$, and $2.9 \times 10^6 \text{ m}^2 / \text{m}^3$, respectively. Diffusible hydrogen content (w_H) in the surface regions with thickness of 10 μm was calculated by the values shown in **Table 4.1**: 27.7 wt ppm in the coarse-grained specimen, and 21.1 wt ppm in the ultrafine-grained, respectively. As shown in **Figure 4.5**, the amount of diffusible hydrogen was almost the same in the different grain-sized specimens. However, the corresponding local diffusible hydrogen contents in the unit surface area of grain boundary (x_H^{GB}) are $4.8 \times 10^{-3} \text{ g} / \text{m}^2$, and $6.1 \times 10^{-5} \text{ g} / \text{m}^2$, respectively, which are obtained from a following formula:

$$x_H^{GB} = w_H / S_v \quad (3.6)$$

where x_H^{GB} is the weight content of hydrogen per unit volume of the specimen. All these values are summarized in **Table 4.4**. The result indicated that the hydrogen content per unit grain boundary area decreased with decreasing the mean grain size.

Table 4.4 Summary of the grain size, grain boundary area per unit volume, diffusible hydrogen content in the subsurface region with 10 μm thick, and estimated hydrogen content per unit grain boundary area in the 22Mn-0.6C steel.

Grain size excluding annealing twins, $d / \mu\text{m}$	Grain boundary area per unit volume, $S_v / \text{m}^2 / \text{m}^3$	Local diffusible hydrogen content at the subsurface with 10 μm , $X_H^{all} / \text{wt. ppm}$	Hydrogen content per unit grain boundary area, $x_H^{GB} / \text{g} / \text{m}^2$
44	4.5×10^4	27.7	4.8×10^{-3}
0.69	2.9×10^6	21.1	6.1×10^{-5}

4.4.3 Stress concentration at grain boundaries

Besides the static condition of hydrogen existence, the plastic deformation also plays an important role in hydrogen accumulation. It is known that the diffusible hydrogen atoms tend to accumulate at high stress concentration sites [17]. During deformation, mobile dislocations can pile-up against the grain boundaries and thus give rise to stress concentration. The stress concentration increases with increasing the number of dislocations pile-up at grain boundaries. The amount of dislocations pile-up at grain boundaries decreases with decreasing the grain size. That is to say, in the present study, the amount of dislocations pile-up at grain boundaries was smaller in the ultrafine-grained specimen than that in the coarse-grained specimen. In addition, the pile-up length of slip dislocations in the ultrafine-grained specimen was shorter than that in the coarse-grained specimen, so that the stress concentration by dislocation

pile-up would be lower in the ultrafine grain-sized specimen. The lower stress concentration at grain boundary resulted in the smaller amount of local hydrogen accumulation at grain boundaries in the ultrafine-grained specimen than that in the coarse-grained specimens during plastic deformation in the tensile test.

Accordingly, we conclude that the smaller hydrogen content per unit grain boundary area in the hydrogen charging process and lower hydrogen accumulation at grain boundaries in the deformation process resulting in less sensitivity to hydrogen embrittlement in the ultrafine-grained specimen.

4.5 Conclusions

In the present chapter, the 22Mn-0.6C steel having different mean grain sizes of 21 μm , and 0.58 μm were used to investigate the effect of grain size on the hydrogen embrittlement behaviors by a slow strain rate tensile test and three-point bending test.

1. In the slow strain rate tensile tests, degradation of the ultimate tensile strength and total elongation occurred by hydrogen charging in both the coarse-grained specimen and the ultrafine-grained specimen. On the other hand, the fraction of brittle fracture surfaces decreased with decreasing the grain size. Moreover, in the three-point bending test, the reduction of apparent fracture toughness in the hydrogen-charged specimens was suppressed by grain refinement. That is to say, hydrogen embrittlement susceptibility was lower in the ultrafine-grained 22Mn-0.6C steel.
2. The diffusible hydrogen content per unit grain boundary area decreased with decreasing the mean grain size. In addition, the degree of local hydrogen accumulation at grain boundary caused by stress concentration during plastic deformation would be smaller in the ultrafine-grained specimen. The above mentioned two factors were considered to be the reasons for the suppression of hydrogen embrittlement by grain refinement in the 22Mn-0.6C steel.

4.6 References

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Chapter 5 Hydrogen-related crack initiation and propagation behaviors of high-manganese austenitic steels

5.1 Introduction

Several papers reported that hydrogen embrittlement occurred in high-manganese austenitic steels [1-7]. In addition, **Chapter 3** and **Chapter 4** of the present thesis confirmed that, hydrogen embrittlement also occurred in the high-manganese austenitic steels, Fe-31Mn-3Al-3Si and Fe-22Mn-0.6C. We also found that the grain refinement suppressed hydrogen embrittlement. Deformation twinning is a characteristic deformation mode in high-manganese steels with low stacking fault energy. Koyama et al. investigated the effect of deformation twinning on hydrogen-assisted cracking in a high-manganese austenitic steel with a chemical composition of 18Mn-1.15C (wt. %) [8]. Their results indicated that the hydrogen-assisted cracking was initiated at both grain boundaries and deformation twin boundaries. Also, crack propagation occurred along both types of boundaries. Understanding the initiation and propagation of hydrogen-related cracks is important for revealing the mechanism of hydrogen embrittlement in high-manganese steels.

In this chapter, the hydrogen-related crack initiation and propagation are

investigated from a viewpoint of microstructural features in the two kinds of high-manganese austenitic steels with various grain sizes.

5.2 Experimental procedure

5.2.1 Materials

The materials used in this chapter were the high-manganese austenitic steels (Fe-31Mn-3Al-3Si, Fe-22Mn-0.6C), which were also used in **Chapter 3** and **Chapter 4**. The detailed chemical compositions of these steels were shown in **Table 2.2** and **Table 2.3**, respectively.

In **Chapter 2**, the coarse-grained specimen ($d = 19 \mu\text{m}$) and the ultrafine-grained specimen ($d = 0.56 \mu\text{m}$) of the 31Mn-3Al-3Si steel, and the coarse-grained specimen ($d = 21 \mu\text{m}$) and the ultrafine-grained specimen ($d = 0.58 \mu\text{m}$) of the 22Mn-0.6C steel were fabricated. These specimens were used in this chapter.

5.2.2 Hydrogen pre-charging

Hydrogen was introduced into the tensile test specimens by electrochemical charging in a solution of 3 % NaCl + 3 g / L NH_4SCN at a current density of $100 \text{ A} / \text{m}^2$ for 172.8 ks (48 h) at room temperature.

5.2.3 Interrupted slow strain rate tensile test

In order to clarify the relationship between crack formation and microstructure, double-notch tensile test specimens were used in this study. The dimension of the tensile test specimen is shown in **Figure 5.1**. Round notches with a diameter of 1 mm and a depth of 1.25 mm were introduced at the center of the gauge part.

After the hydrogen charging completed, an uniaxial slow strain rate tensile test was conducted using a tensile machine (Shimadzu, AG-X plus, 100 kN) at a crosshead speed of 5×10^{-3} mm / min, corresponding to an initial strain rate of 8.3×10^{-6} / s at room temperature. To observe the early deformation of cracks before fracture, tensile test was interrupted immediately after the maximum stress.

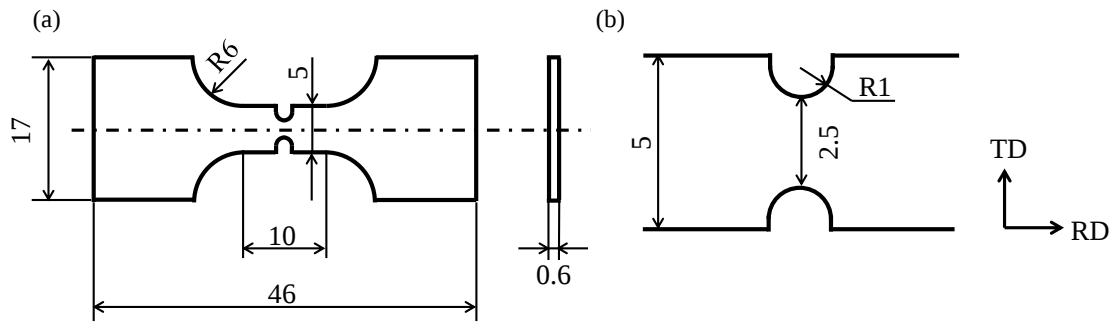


Figure 5.1 Schematic illustration of the double-notch tensile test specimen (a) and magnified view around the notch part (b).

5.2.4 hydrogen-related crack and microstructure observation

After the slow strain rate tensile test, the gauge part of the double-notch tensile test specimen was cut out and polished. In order to prevent the preferential etching around the cracks, vibratory polishing (Buehler, Vibromet 2) was conducted instead of electro-polishing. The surface cracks and microstructures were characterized by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7800F) and electron back-scattering diffraction (EBSD) analysis attached in the SEM (JEOL JSM-7100F) operated at an accelerating voltage of 15 kV. The cracks were observed from the normal direction (ND) of the sheet. The EBSD measurement was performed using TSL OIM data collection system, and the obtained EBSD data were analyzed by TSL OIM analysis software.

5.3 Results and discussion

5.3.1 31Mn-3Al-3Si high-manganese austenitic steel

5.3.1.1 Interrupted slow strain rate tensile tests of double-notch specimens

Figure 5.2 shows stress-displacement curves of the hydrogen-charged 31Mn-3Al-3Si steel with different grain sizes. The stress was calculated by the area of the cross section at the notch root. Both tensile tests were interrupted just after the maximum stresses before fracture. The tendency of the strength and elongation in the notched-specimens is the same as that in the smooth specimens shown in **Figure 3.6**.

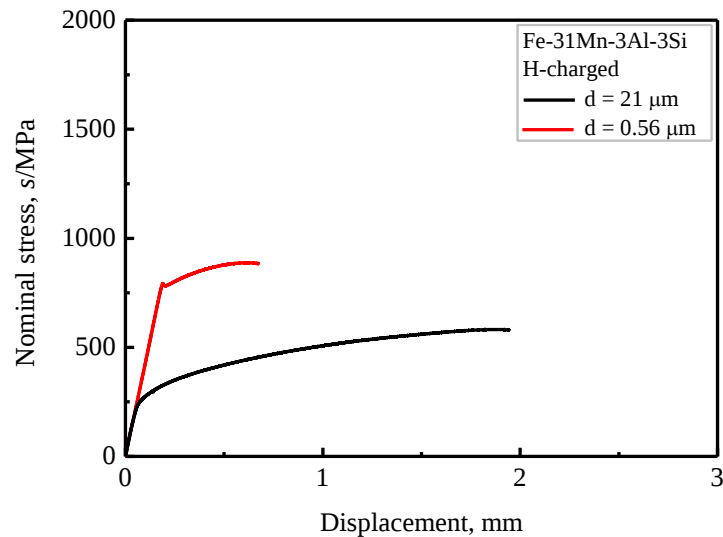


Figure 5.2 Stress-displacement curves of hydrogen-charged the 31Mn-3Al-3Si steel with different grain sizes. Tensile tests were interrupted after the maximum stresses.

5.3.1.2 Observation of hydrogen-related cracks

Deformation is not uniform in the tensile test specimen during tensile test when there is a notch at the gauge part, because of the stress concentration around the notch root. And cracks generate from the stress concentration site. **Figure 5.3** shows SEM images around the notch root of the hydrogen-charged tensile test specimen of the 31Mn-3Al-3Si steel with different grain sizes after stopping the tensile test at the maximum stresses.

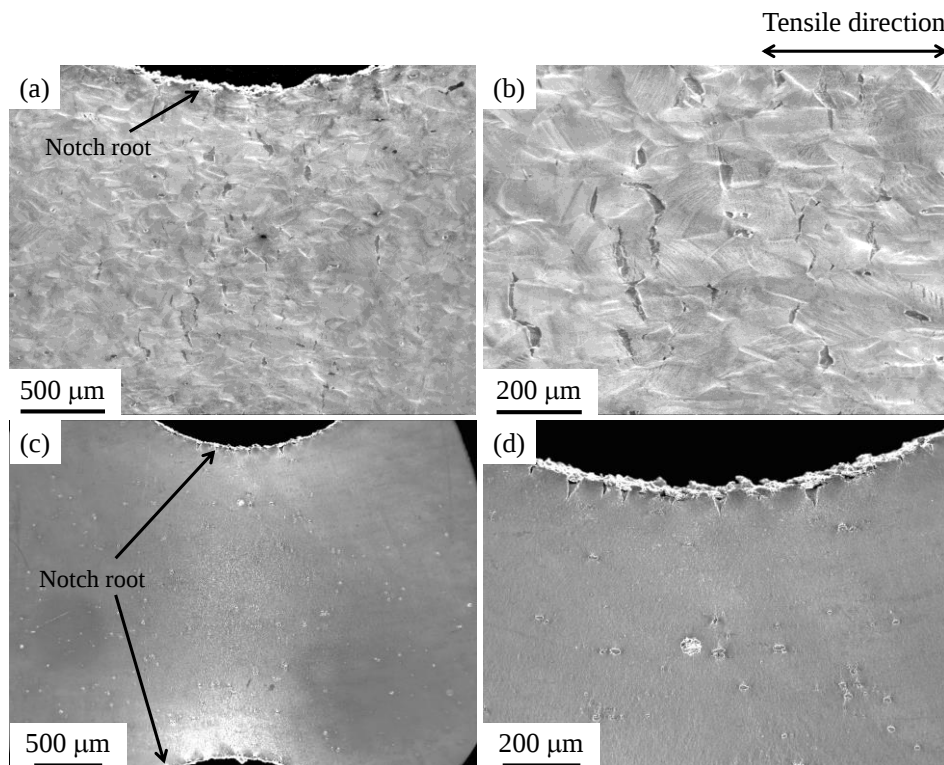


Figure 5.3 SEM images around the notch root of the hydrogen-charged 31Mn-3Al-3Si specimen after stopping at the tensile test at the maximum stresses: (a), (b) the hydrogen-charged coarse-grained specimen. (c), (d) the hydrogen-charged ultrafine-grained specimen.

In the hydrogen-charged coarse-grained specimen, some hydrogen-related cracks have already formed around the notch root. These cracks were teared along the tensile direction by the subsequent deformation. In contrast, relatively small and a few hydrogen-related cracks were observed in the ultrafine-grained specimen.

5.3.2 22Mn-0.6C high-manganese austenitic steel

5.3.2.1 Interrupted slow stain rate tensile tests of double-notch specimens

Figure 5.4 shows the stress-displacement curves of the hydrogen-charged 22Mn-0.6C steel with different grain sizes. The tensile tests were stopped at different displacements: (a), and (b) are the hydrogen-charged coarse-grained specimen and the hydrogen-charged ultrafine-grained specimen stopped immediately after reaching the maximum stress. The tensile test of the hydrogen-charged coarse-grained specimen was also stopped at the same displacement (i.e., the displacement of 0.59 mm in **Figure 5.4** (b)) as that for the ultrafine-grained one, as shown in **Figure 5.4** (c).

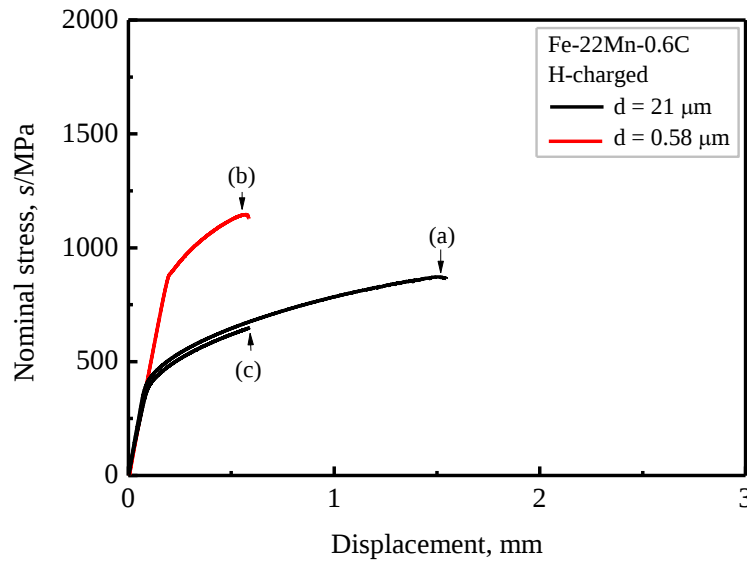


Figure 5.4 Stress-displacement curves of the hydrogen-charged 22Mn-0.6C steel obtained from interrupted tensile test: (a) the coarse-grained specimen stopped at the maximum stress (displacement of 1.54 mm), (b) the ultrafine-grained specimen stopped at the maximum stress (displacement of 0.59 mm), and (c) the coarse-grained specimen stopped at the same displacement as that for the ultrafine-grained specimen (displacement of 0.59 mm).

5.3.2.2 Observation of hydrogen-related cracks

Figure 5.5 shows SEM images around the notch root of the uncharged 22Mn-0.6C steel specimens with different grain sizes after stopping the tensile test at the maximum stresses. Only a few cracks were observed around the notch roots in both the uncharged coarse-grained specimens and the uncharged ultrafine-grained specimens. It was found that the crack length was less than hundred micro-meters.

Figure 5.6 shows SEM images around the notch root of the hydrogen-charged

22Mn-0.6C steel specimens with different grain sizes. Compared with the uncharged specimens, large numbers of cracks were observed in the corresponding hydrogen-charged specimens. Around the notch root, a large number of cracks were observed at the specimen surface just before fracture in the tensile test (**Figure 5.6 (a)**). **Figure 5.6 (b)** shows the magnified image of (a). It is noteworthy that the hydrogen-related cracks propagated perpendicular to the tensile axis. A large amount of hydrogen-related cracks have a length of more than hundred micro-meters. In the case of the hydrogen-charged ultrafine-grained specimen (**Figure 5.6 (c)**), several large cracks were observed at the notch root. In the magnified image (**Figure 5.6 (d)**), numerous numbers of hydrogen-related cracks with length smaller than one micro-meter were observed as well as several long cracks. Length of the hydrogen-related cracks observed around the notch roots of the hydrogen-charged specimens is summarized in **Figure 5.7**. According to **Figure 5.7**, the crack length was much larger in the hydrogen-charged coarse-grained specimen than that in the hydrogen-charged ultrafine-grained specimen. This indicates that the size of the hydrogen-related cracks decreased with decreasing the grain size.

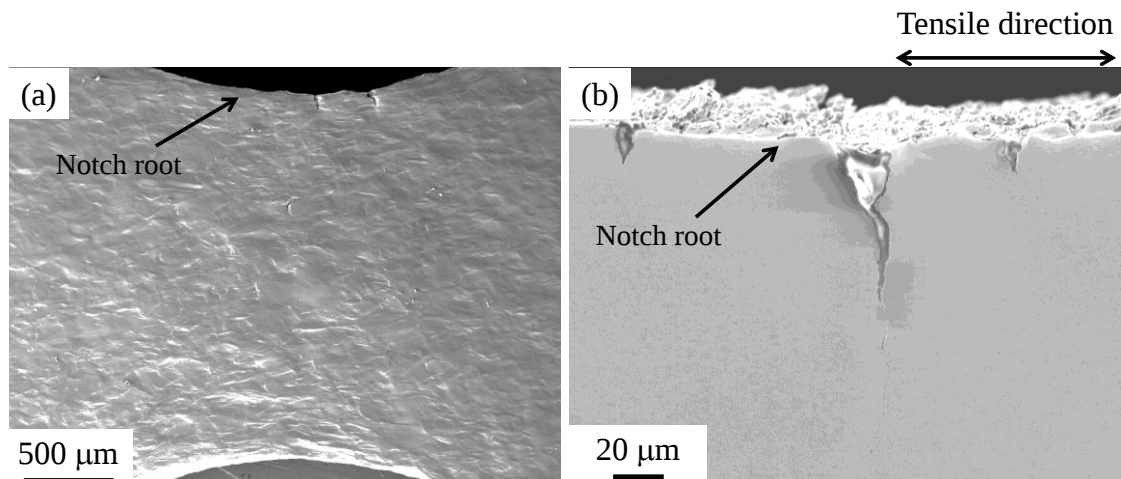


Figure 5.5 SEM images around the notch root after interrupted tensile test in the 22Mn-0.6C steel: (a) the uncharged coarse-grained specimen, and (b) the uncharged ultrafine-grained specimen.

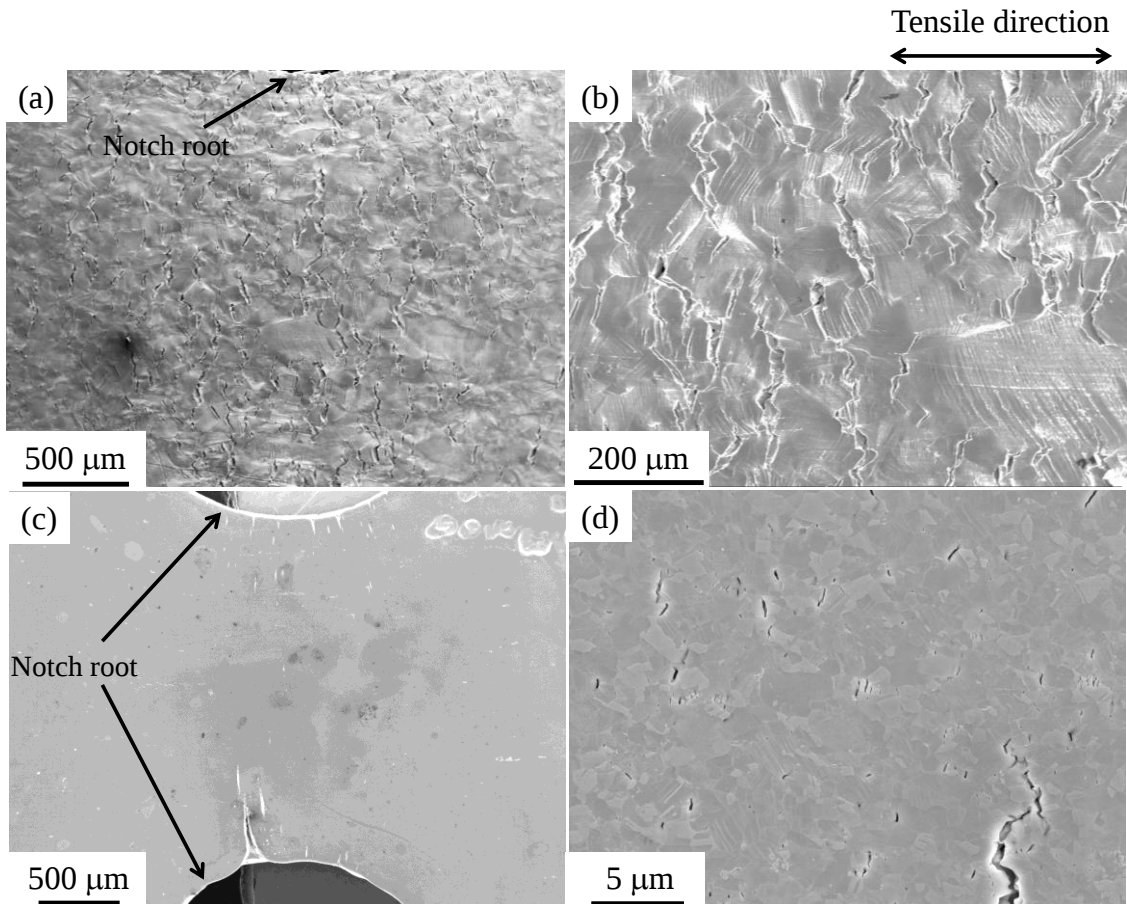


Figure 5.6 SEM images around the notch root of the hydrogen-charged 22Mn-0.6C steel after interrupting the tensile test at the maximum stress: (a), (b) the hydrogen-charged coarse-grained specimen. (c), (d) the hydrogen-charged ultrafine-grained specimen.

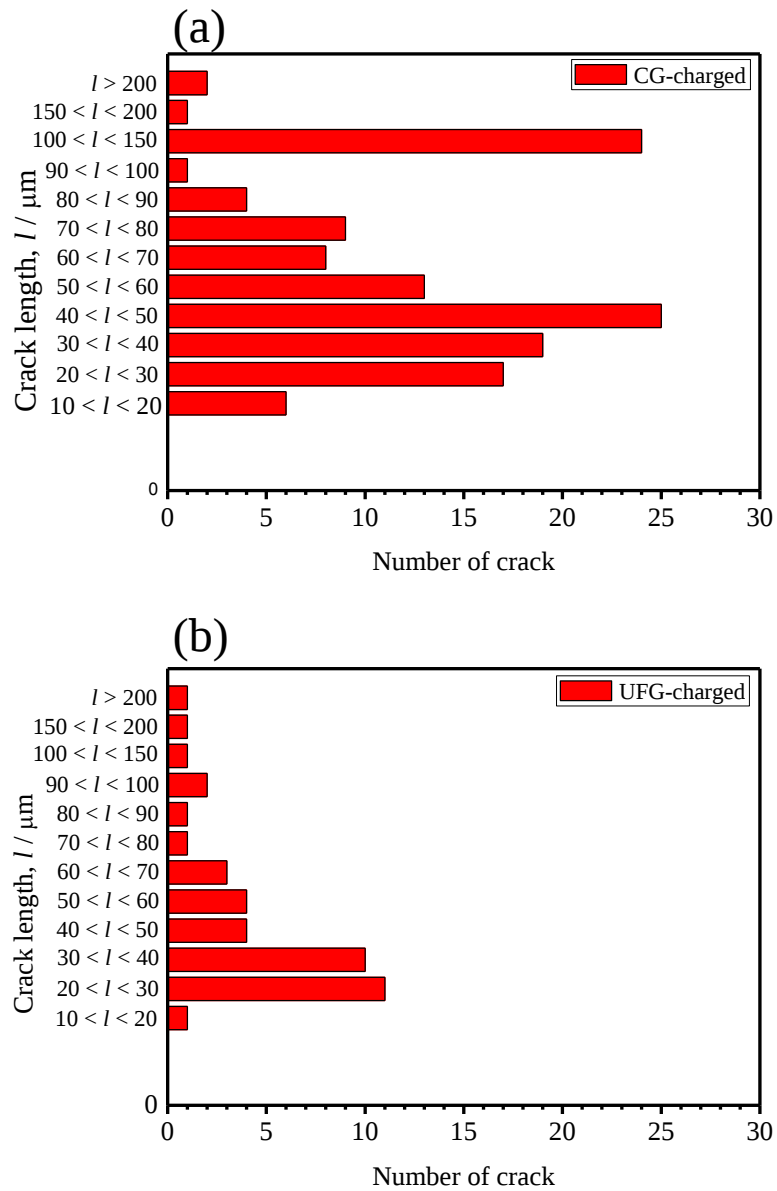


Figure 5.7 Length distributions of the hydrogen-related cracks observed around the notch root of the hydrogen-charged 22Mn-0.6C steel: (a) the coarse-grained specimen, (b) the ultrafine-grained specimen.

The tensile test of the hydrogen-charged coarse-grained specimen was interrupted at the same displacement as that in the ultrafine-grained one (at the displacement of 0.59

mm), as shown in **Figure 5.4** (c). The SEM images around the notch root are shown in **Figure 5.8**. A certain number of hydrogen-related cracks have already propagated at the early stage of deformation in the hydrogen-charged coarse-grained specimen.

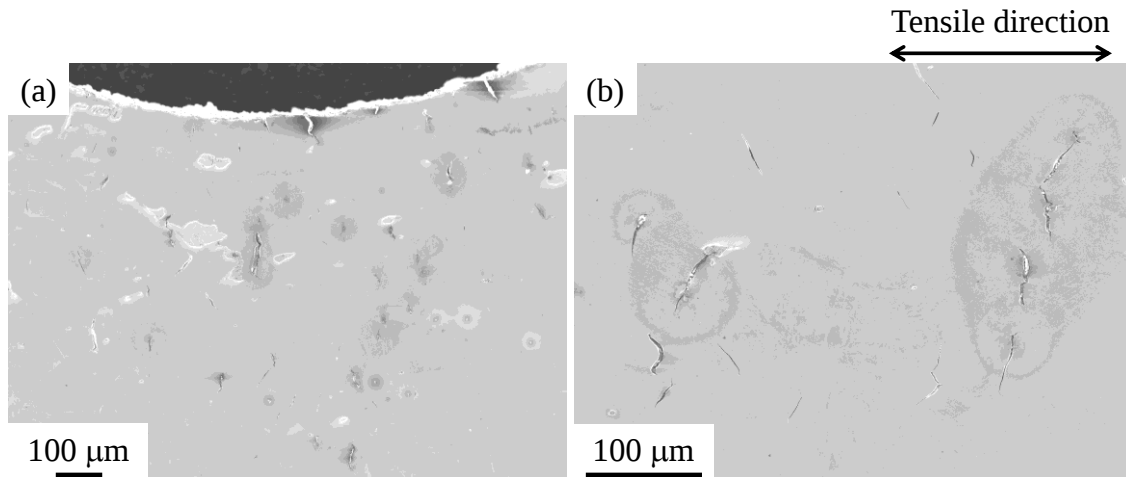


Figure 5.8 SEM images around the notch root of the hydrogen-charged coarse-grained 22Mn-0.6C specimen. The tensile test was stopped at the same displacement as the ultrafine-grained specimen (displacement of 0.59 mm).

5.3.2.3 Microstructural characterization of hydrogen-related cracks

An EBSD scanning was also conducted on the region around the hydrogen-related cracks to characterize the relationship between microstructure and crack initiation.

Figure 5.9 (a, c, e) show SEM images, and **Figure 5.9** (b, d, f) show EBSD orientation maps of the typical cracks formed in the hydrogen-charged coarse-grained 22Mn-0.6C steel, whose tensile test was stopped at the maximum stress.

In **Figure 5.9** (a), (b), the crack formed at the grain boundary, where deformation twins impinged. On the other hand, the crack shown in **Figure 5.9** (c), (d) formed inside the grain in which there were many deformation twins. The crack shown in **Figure 5.9** (e), (f) had length over hundred micro-meters, which propagated along the grain boundaries. In all the cases where the cracks formed at the grain boundaries, deformation twins impinged at the grain boundaries.

Figure 5.10 shows SEM image and EBSD orientation map around the crack in the hydrogen-charged ultrafine-grained 22Mn-0.6C steel, whose tensile test was stopped at the maximum stress. It was found from **Figure 5.10** that the crack formed at the grain boundaries.

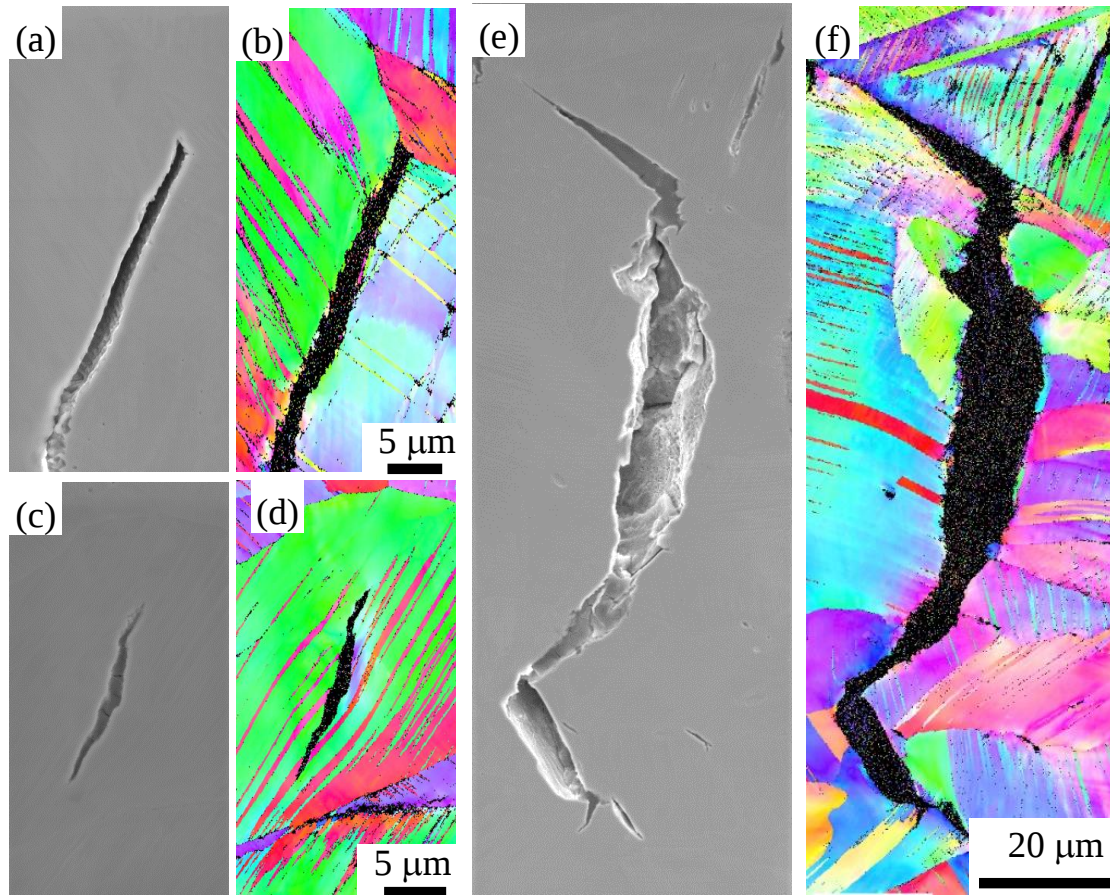


Figure 5.9 SEM images (a, c, e), and EBSD orientation maps (b, d, f) of the typical cracks formed in the hydrogen-charged coarse-grained 22Mn-0.6C specimen whose tensile test was stopped at the maximum stress.

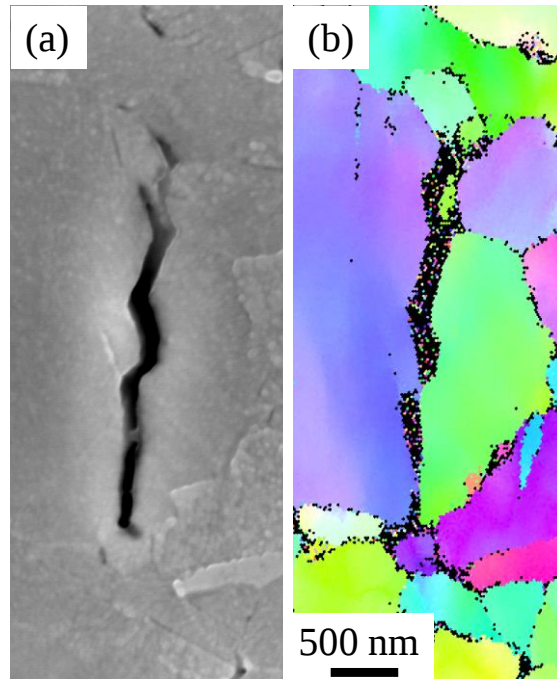


Figure 5.10 SEM image (a) and EBSD (b) orientation map of the hydrogen-charged ultrafine-grained 22Mn-0.6C specimen whose tensile test was stopped at the maximum stress.

The cracks formed in the hydrogen-charged coarse-grained specimen, whose tensile test was stopped at the same displacement (0.59 mm) as that for the ultrafine-grained one, were also examined by EBSD. **Figure 5.11** shows EBSD orientation maps of three typical cracks that observed in the hydrogen-charged coarse-grained specimen: (a) the crack formed at the grain boundaries, (b) the crack propagated along the grain boundaries and some parts propagated inside the grain, and (c) the crack formed at the annealing twin boundary. Totally 47 cracks around the notch root were observed by EBSD, and the results are summarized in **Table 5.1**. It

was found from **Table 5.1** that almost all the hydrogen-related cracks formed at grain boundaries. On the other hand, no hydrogen-related crack formation and propagation was observed in the 22Mn-0.6C steel.

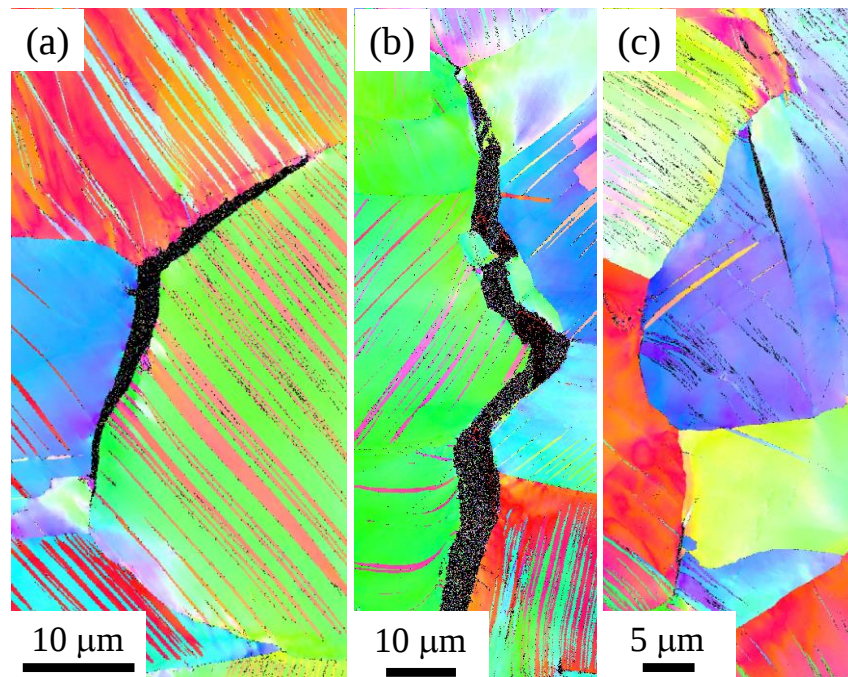


Figure 5.11 EBSD orientation maps around cracks in the hydrogen-charged coarse-grained 22Mn-0.6C specimen whose tensile test was interrupted at the same displacement as that for the ultrafine-grained specimen: (a) the crack formed at the grain boundaries, (b) the crack propagated along the grain boundaries and some parts propagated inside the grain, and (c) the crack formed at the annealing twin boundaries.

Table 5.1 Summary of the crack formation and propagation sites in the hydrogen-charged coarse-grained 22Mn-0.6C specimen whose tensile test was stopped at the same displacement as that for the hydrogen-charged ultrafine-grained specimen.

Crack formation and propagation site	At grain Boundary	Mixture of propagation along grain boundary and inside of grain	Annealing twin boundary
Number of cracks	42	2	3

In the case of the hydrogen-charged specimens whose tensile tests were interrupted at the maximum stresses, the length of hydrogen-related cracks in the ultrafine-grained specimens was shorter than that in the coarse-grained specimen (**Figure 5.6**). Furthermore, a large amount of cracks having length of several ten micro-meters have already existed in the hydrogen-charged coarse-grained specimen at the early deformation stage (**Figure 5.8**). As mentioned in **Chapter 4**, the diffusible hydrogen content per unit grain boundary area and hydrogen accumulation in the ultrafine-grained specimen was lower than that in the coarse-grained specimen. Accordingly, the crack formation and propagation was suppressed in the ultrafine-grained specimen due to the low hydrogen concentration per unit grain boundaries area. In addition, the microstructural characterization of the cracks suggests that the cracks formed at grain boundaries, which emphasized the important role of grain boundaries on the hydrogen embrittlement behavior in the 22Mn-0.6C steel.

5.4 Conclusions

Hydrogen-related cracks around the notch root of the hydrogen-charged 31Mn-3Al-3Si and 22Mn-0.6C steel specimens, whose tensile tests were stopped at different displacements, were characterized by SEM-EBSD.

1. In the 31Mn-3Al-3Si steel, at the stage of just before fracture, the number of hydrogen-related cracks in the ultrafine-grained specimen was smaller than that in the coarse-grained specimen.
2. In the 22Mn-0.6C steel specimens whose tensile tests were stopped at the maximum stresses, a large amount of hydrogen-related cracks were observed in both the coarse-grained specimen and the ultrafine-grained specimens. However, the crack length in the coarse-grained specimen was much larger than that in the ultrafine-grained specimen. Hydrogen-related cracks have already formed at the earlier stage of deformation in the hydrogen-charged coarse-grained specimen.
3. The microstructural characterization of the hydrogen-related cracks in the 22Mn-0.6C steel revealed that most of the cracks formed and propagated at the grain boundaries, which confirmed an important role of grain boundaries in the hydrogen embrittlement.

5.5 References

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Chapter 6 Summary and conclusions

In this thesis, cold rolling and subsequent annealing was utilized to fabricate various grain-sized 31Mn-3Al-3Si and 22Mn-0.6C high-manganese austenitic steels of which mean grain sizes ranged from 21 μm to 0.56 μm . Effects of the grain size on hydrogen embrittlement behaviors in the two kinds of high-manganese austenitic steels were investigated. The results obtained in the present thesis are summarized as follows.

Chapter 1 introduced the background of the present research. High-manganese austenitic steels, hydrogen embrittlement behaviors, grain refinement were reviewed, and the objective of the present study was raised.

In Chapter 2, the as-received 31Mn-3Al-3Si high-manganese austenitic steels were cold-rolled to total thickness reduction of 92% and subsequently annealed at temperatures ranging from 650 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ for different periods. As a result, fully recrystallized microstructures involving a large amount of annealing twins were obtained. The mean grain sizes including annealing twin boundaries ranged from 0.56 μm to 19 μm . After four-stage of cold-rolling (with a total thickness reduction of 92%) and annealing treatment at 550 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$, the coarse-grained 22Mn-0.6C austenitic

steel with a mean grain size of 21 μm in the starting material was refined to 0.58 μm and 2.4 μm including annealing twins, respectively. The fully recrystallized ultrafine grained microstructures with mean grain sizes smaller than 1 μm could be successfully fabricated by conventional cold rolling and subsequent annealing treatments for the first time.

In **Chapter 3**, hydrogen embrittlement behaviors of the hydrogen pre-charged 31Mn-3Al-3Si high-manganese austenitic steel having different grain sizes were investigated by a slow strain rate tensile test at room temperature. The diffusible hydrogen content was measured after the hydrogen charging process. As a result, it was found that diffusible hydrogen content increased with decreasing the grain size. In the tensile test, the yield strength and ultimate tensile strength were not influenced by hydrogen charging. However, the total elongation and apparent work hardening rate decreased significantly at the later stage of deformation in the hydrogen-charged coarse-grained specimen compared with the uncharged one. In the case of the ultrafine-grained specimen, the total elongation was almost the same in the hydrogen-charged and uncharged specimens. The result indicated that hydrogen embrittlement was suppressed by grain refinement. The fracture surfaces consisted of dimples, which indicated ductile fracture in all the specimens.

In **Chapter 4**, the hydrogen embrittlement behaviors of the hydrogen pre-charged 22Mn-0.6C austenitic steel with different grain sizes of 21 μm and 0.58 μm were investigated by a slow strain rate tensile test at room temperature. The diffusible hydrogen content was almost the same in both the coarse-grained specimen and the ultrafine-grained specimen. In the tensile test, the yield strength was not influenced by hydrogen charging. However, the total elongation and the ultimate tensile strength decreased significantly in the hydrogen-charged specimens with different grain sizes. The work hardening rate curves indicated that both hydrogen-charged specimens fractured before reaching the plastic instability condition. However, the fracture surfaces consisted of ductile fracture and brittle fracture surfaces and the fraction of brittle fracture surfaces reduced significantly from 8.6 % in the coarse-grained specimen to 0.6 % in the ultrafine-grained specimen. Furthermore, the comparison of the fracture toughness obtained from a three-point bending test suggested that the reduction of fracture toughness in the hydrogen-charged specimens was suppressed by grain refinement. The results indicated that hydrogen embrittlement susceptibility reduced by grain refinement in the 22Mn-0.6C austenitic steel.

Although the hydrogen embrittlement behaviors had some differences in two kinds of high-manganese austenitic steels in **Chapter 3** and **Chapter 4**, both steels showed

similar tendency that hydrogen embrittlement was suppressed by grain refinement. The reason for this is that the diffusible hydrogen content per unit grain boundary area and hydrogen accumulation at grain boundaries decreased with decreasing the grain size in both kinds of steels.

In **Chapter 5**, interrupted tensile test at various displacements during a slow strain rate tensile test were conducted using hydrogen-charged double-notch tensile test specimens, and the hydrogen-related crack initiation and propagation behaviors were investigated by SEM-EBSD. Tensile tests were stopped at the maximum stresses in the 31Mn-3Al-3Si austenitic steel with different grain sizes. Several cracks were observed in the coarse-grained specimen, whereas the crack number and crack length decreased in the ultrafine-grained specimen. In the 22Mn-0.6C austenitic steel, a large amount of hydrogen-related cracks were observed in both different grain-sized specimens, for which tensile tests were interrupted at the maximum stresses. However, the crack length was much larger in the coarse grain-sized specimen than that in the ultrafine-grained specimens. Tensile tests of the coarse-grained specimen were also interrupted at the same displacement as that at the maximum stress in the ultrafine-grained specimen. The result showed that a certain number of hydrogen-related cracks having length of several tens micro-meters have already existed

around the notch root at the early stage of deformation. Microstructural characteristics of the hydrogen-related cracks were also investigated and most of the cracks initiated and propagated along grain boundaries in the coarse-grained and ultrafine-grained 22Mn-0.6C austenitic steel, which clearly indicated that the grain boundary played a key role in the hydrogen embrittlement behaviors.

Chapter 6 concluded the new finding in the present research work.

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List of publications

International journal papers

- (1) Enhanced strength and ductility in an ultrafine-grained Fe-22Mn-0.6C austenitic steel having fully recrystallized structure
Yanzhong Tian, **Yu Bai**, Meichuan Chen, Akinobu Shibata, Daisuke Terada, Nobuhiro Tsuji
Metallurgical and Materials Transactions A: 45 (2014) 5300-5304.
- (2) Effect of grain refinement on hydrogen embrittlement behaviors of a high-Mn TWIP steel
Yu Bai, Yuji Momotani, Meichuan Chen, Akinobu Shibata and Nobuhiro Tsuji
Submitted to *Materials Science and Engineering A*.

International proceeding papers

- (1) Hydrogen embrittlement behaviors of ultrafine-grained TWIP steel
Yu Bai, Akinobu Shibata, Daisuke Terada, Nobuhiro Tsuji
2nd International Conference on High Manganese Steel 2014, (2014-9) 295-298.