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Role of ε martensite in tensile properties and hydrogen degradation of high-Mn steels

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ABSTRACT

Effects of ε martensite on tensile properties and hydrogen degradation behaviors of a high Mn steel were investigated. For this purpose, a Fe–15Mn–2Cr–0.6C steel containing various amount of ε martensite was prepared and tensile tested at room temperature. Microstructures were examined by electron back scattered diffraction and transmission electron microscopy. Then, a series of electrochemical hydrogen pre-charging, slow strain rate tests, and thermal desorption spectrometry (TDS) analyses was conducted to examine the hydrogen degradation behaviors. Deformation of the steel without ε martensite (i.e. fully austenitic) was dominated by slip and mechanical twinning, but that of the steel containing ε martensite was mainly attributed to transformation induced plasticity in association with strain induced martensitic transformation during deformation, resulting in higher work hardening rate. However, tensile strength and elongation on the steel containing ε martensite were lower than those of the fully austenitic steel, since cracks were prone to be initiated and propagated at the region of ε martensite which is harder than austenite. Furthermore, it was found that ε martensite provided many diffusible hydrogen trapping sites. Consequently, the notch fracture stress of the steel containing ε martensite decreased significantly as the diffusible hydrogen content increased. The activation energy for hydrogen detrapping from its trapping sites was also calculated by means of the TDS analyses, ~22 kJ/mol for the γ/ε interfaces, and ~37 kJ/mol for dislocations/γ grain boundaries.

1. Introduction

Hydrogen embrittlement (HE) has been investigated in various metals and alloys, and its mechanisms are well documented in the literature [1,2]. HE of high strength steels is of increasing interest because the susceptibility to HE is known to increase as the strength increases. In general, HE is influenced by microstructural factors (crystal structure, carbon content and various defects) and by mechanical factors such as the stress gradient and strain rate [3–7]. Of these, defects are considered important in HE because they act as the hydrogen trapping sites by interacting with hydrogen, leading to either decrease or increase of the HE susceptibility. There are generally two types of hydrogen trapping sites. One is the diffusible or reversible trapping sites with the low activation energy for detrapping, such as grain boundaries [3], dislocations [8] and coherent carbide interfaces [9]. HE is primarily caused by hydrogen at these diffusible trapping sites. Another is the non-diffusible or irreversible trapping sites with the high energy barriers for detrapping, such as inclusions [10], voids [11] and incoherent carbide interfaces [9]. These non-diffusible trapping sites are not responsible for HE.

Austenitic twinning induced plasticity (TWIP) steels are being developed as the advanced automotive structural steel due to their excellent combinations of strength and ductility [12]. Especially, the high Mn TWIP steel containing 0.6% C exhibits very high strength and excellent ductility [13]. Nevertheless, its application to the automotive parts is limited because of hydrogen delayed fracture in association with the combined effects of the presence of transformed ε martensite and internal residual stress [14]. Although there are numerous documents regarding the effects of ε martensite on mechanical properties of the high Mn steels [15–20], little systematic information is available on its role on hydrogen degradation in this steel grade such as hydrogen trapping at the γ austenite/ε martensite interfaces, the effects of the ε martensite amount, which is essential to achieve successful application of the high Mn TWIP steel.

ε martensite is to be formed by heat treatment [21,22] and by deformation of austenite with the relatively low stacking fault

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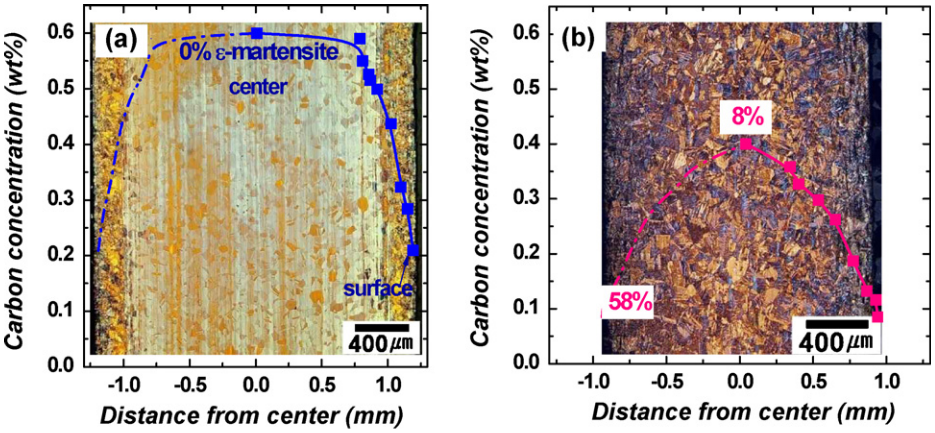

Fig. 1. The color-etched microstructure of Fe–15Mn–2Cr–0.6C (wt.%) steel and corresponding C concentration profile annealed at 1000 °C for different times: (a) 15 min annealing – fully austenitic at the center and (b) 180 min – formation of various amount of ε martensite ranging from 58% at the center to 8% at the surface by decarburization. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

energy. The aim of the present work is to study how hydrogen degradation of high strength TWIP steel is affected by ε martensite which might be formed during heat treatment. For this purpose, a series of electrochemical hydrogen pre-charging, slow strain rate test (SSRT) and thermal desorption spectrometry (TDS) analyses were conducted on a high Mn TWIP steel with various volume fractions of ε martensite.

2. Experimental procedure

A high-Mn TWIP steel of 15Mn–2Cr–0.6C (wt.%) was prepared in the form of 5 mm-thick hot-rolled plates. They were cold-rolled to a final thickness of 2.5 mm, annealed at 1000 °C for either 15 min or 180 min in the air, and then air-cooled to room temperature. During annealing, surface decarburization occurred, and it accompanied thermal distortion which induced ε martensite transformation. The decarburization depth from the plate surface, i.e. the ε martensite amount, varied with the annealing conditions, and therefore it was possible to prepare the samples with various amount of ε martensite. As will be described in the next section in detail, the fully austenitic sample with no ε martensite were taken from the center of the plates annealed for 15 min, and the samples with ∼8% ε martensite and ∼58% ε martensite were taken from the center and the surface of the plates annealed for 180 min.

To reveal the as-annealed microstructures clearly, a series of etching was employed: 4% nital for 30 s, 10% HCl in ethanol for 2 s, and 10% sodium metabisulphite in distilled water for 10 s [23]. The amount of body-centered cubic (bcc) α or hexagonally close-packed (hcp) ε martensite was quantified using electron back scattered diffraction (EBSD) (FEI Helios/Pegasus) [24]. In preparing the EBSD samples, electropolishing was carried out to eliminate α or ε martensite formed by mechanical polishing [25]. Transmission electron microscope (TEM) images were taken on a Cs-corrected high-resolution TEM (JEOL JEM-2100F) at 200 kV with the samples prepared by a focused ion beam.

Tensile tests were conducted at a strain rate of 5×10^{-3}/s using the ASTM E8M subsize specimen with the gauge dimensions of 25 mm length and 6 mm width. In order to examine the hydrogen degradation behavior, slow strain rate tests (SSRTs) were conducted on the notched samples after hydrogen charging. The notch can help the hydrogen mobility increase in the steel during loading. 60° notch of 1 mm depth was made in the center of the gauge section, using a wire machine ($R = 0.25$ mm). The calculated stress intensity factor of the notch was 4.37. Hydrogen charging on the samples with the different amount of ε martensite was performed in an aqueous solution of 3 mass% NaCl and 0.3 mass% NH_4SCN [26]. Hydrogen charging by the electrochemical method is known to be sensitive to the surface roughness, so the sample surface was ground using sand paper (#400 to #1500). During electrochemical charging, the current density was fixed at 60 A/m^2 and the charging time was varied from 48 h to 120 h. The charged samples were coated with Cd, which is as an effective barrier to emission of hydrogen during subsequent mechanical tests. SSRTs were performed using an INSTRON 8501 machine at a stroke speed of 0.01 mm/min (strain rate of 1.7×10^{-4}/s). After SSRTs, the Cd coating layer was removed and the hydrogen content was analyzed by a thermal desorption spectroscopy (TDS) equipped with a gas chromatograph (Agilent GC 7890A). During the TDS analyses, the sample was heated to 500 °C at 100 °C/h and the emitted gas was collected at the 5 min intervals under continuous He gas flow.

3. Results

3.1. As-annealed microstructures

Fig. 1 shows the thickness view of the as-annealed steels plates and the corresponding carbon concentration profile measured by a spark emission method after removing a 100 μm layer from the sample surface. As aforementioned, the decarburized depth was strongly affected by the annealing time. For the 15 min annealed sample (Fig. 1a), except the decarburized surface layers on both sides, the C content of the center area of the plate was ∼0.6% in agreement with its initial bulk concentration. The decarburized depth was ∼400 μm and the carbon concentration drastically decreased towards the surface. As the annealing time increased to 180 min (Fig. 1b), the C concentration of the whole section was less than the initial one: the maximum of ∼0.4% at the center and the minimum less than 0.1% at the surface. That is, severe decarburization occurred even at the center by 180 min annealing. In contrast to the C distribution, the thickness wise distribution of major alloying elements of Mn and Cr was uniform with their initial concentration.

Color etched optical microstructures in the selected area of both samples are shown in Fig. 2. The center area of the plate annealed for 15 min (∼0.6%C) revealed fully austenitic with annealing twins (Fig. 2a). The center area of the plate annealed for 180 min (∼0.4%C) and the surface layer of the same plate (<0.1%C), Fig. 2b and c respectively, exhibited austenite grains with a fine band structure (mostly, ε martensite). The constituent phases and their fractions of each sample were analyzed from the corresponding image quality maps and phase maps obtained from EBSD and the TSL-OIM software. The