

**Utilizing Multi-Scale Modeling and Experimentation to Uncover
the Role of Micro-Deformation Mechanisms on the Performance
of High-Strength Steels**

by

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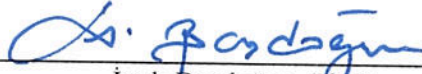
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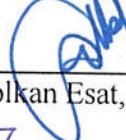
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ABSTRACT

The first aim of the work presented herein is to investigate the composition and temperature dependencies of deformation response of high-manganese austenitic steels under high-velocity tensile, compressive and impact loading scenarios with a focus on micro-scale deformation mechanisms. The promotion of twinning deformation under high-velocity loading over the slip-twin interactions usually observed in low-velocity loading conditions was comprehensively examined with optical microscopy, confocal laser scanning microscopy, scanning electron microscopy and transmission electron microscopy. In addition, thermal analysis of plastic deformation was carried out by in-situ thermal imaging. The current findings clearly demonstrate that the formation of nano-twins within the primary twins constitutes a significant contribution to the strain hardening response of high-manganese austenitic steels. Overall, the current results shed light on the complicated work hardening mechanisms prevalent in high-manganese austenitic steels utilizing high-velocity deformation experiments.

The investigation of micro-deformation mechanisms in high-manganese austenitic steels was extended by modeling the contributions of dynamic strain aging on the unique hardening response of this class of steels, as well as hydrogen interstitial effects on hydrogen storage materials. For these purposes, a new multi-scale modeling approach was proposed. Specifically, for dynamic strain aging modeling, a unique hardening model was proposed that can compute the shear stress contribution of carbon atom and incorporates it to the classical Voce hardening. The proposed model is capable of predicting the role of dynamic strain aging and resulting negative strain rate sensitivity on the deformation response of Hadfield steel. For modeling the hydrogen interstitial effects on the overall hardening response of hydrogen storage materials, classical crystal plasticity scheme was modified to account for the shear stress imposed on arrested dislocations due to the surrounding hydrogen interstitials. In order

to observe the hydrogen effect experimentally and validate the corresponding model, several tensile tests were conducted to hydrogen-induced samples at a moderate strain rate and at room temperature. The combined experimental and unique modeling effort opens a new venue for predicting the alterations in the performance of metallic hydrogen storage materials, where hydrogen embrittlement is unavoidable.

ÖZET

Burada sunulan çalışmanın ilk amacı, yüksek manganezli östenitik çeliklerin, farklı yüksek hızlı mekanik yükleme şartları altındaki deformasyon davranışlarının incelenmesi ve kimyasal kompozisyon ve sıcaklığın bu davranışlar üzerindeki etkilerinin araştırılmasıdır. Bu doğrultuda, mikroyapı gözlemleri mikro ölçekli deformasyon mekanizmalarına odaklanarak gerçekleştirilmiştir. Düşük deformasyon hızı altında gerçekleşen kayma-ikizleme etkileşimi yerine, yüksek deformasyon hızı altındaki yoğun mekanik ikizlemeler optik mikroskop, derin gören mikroskop, taramalı elektron mikroskobu ve geçirmeli elektron mikroskobu yardımı ile gözlemlenmiştir. Buna ilaveten, yerinde termal kamera kullanımı ile plastik deformasyon sırasındaki ısı değişimi gözlenmiştir. Bu gözlemlerin sonucunda, önceden oluşmuş mekanik ikizlemelerin içerisindeki nano ikizlemelerin yüksek manganezli östenitik çeliklerin gerinim sertleşmesine katkıda bulunduğu gözlemlenmiştir. Sonuç olarak, bahsedilen çalışmanın sonuçları, yüksek manganezli östenitik çeliklerin, yüksek deformasyon hızlı çekme-basma-darbe yüklemeleri altındaki karışık işlem sertleşme mekanizmalarını daha detaylı anlaşılmasını sağlamıştır.

Yüksek manganezli östenitik çeliklerin mikro ölçekli deformasyon mekanizmalarının incelenmesi, Hadfield çeliğinin olağan dışı sertleşme kapasitesine, dinamik germe yaşlandırmasının etkisinin ve hidrojen depolama malzemelerinin mekanik özelliklerine, hidrojen arayer atomunun etkilerinin modellenmeleri ile genişletilmiştir. Bu amaçlar doğrultusunda, yeni bir, çok ölçekli modelleme yöntemi geliştirilmiştir. Spesifik olarak, dinamik germe yaşlandırması çalışmasında, karbon atomlarının kesme gerilimi etkisini geleneksel Voce sertleşme denklemi ile birleştiren, yeni bir sertleşme denklemi önerilmiştir. Önerilen model, dinamik germe yaşlandırmasını ve sonucunda meydana gelen Hadfield çeliklerinin deformasyon davranışındaki negatif gerinim duyarlılığını hesaplayabilmektedir. Hidrojen depolama malzemelerinin mekanik özelliklerine, hidrojen arayer atomunun

etkilerinin modellenmesi çalışmasında, geleneksel kristal plastisite denklemleri, hidrojen kaynaklı oluşan kesme gerilimi etkisini içerecek şekilde tadil edilmiştir. Bahsedilen hidrojen etkisinin deneysel olarak gözlemlenip, modelleme sonuçlarının geçerli kılınabilmesi için, hidrojen içeren malzemelere düşük gerinim hızında ve oda sıcaklığında çekme deneyleri gerçekleştirilmiştir. Gerçekleştirilen deneysel ve modelleme çalışmaları sonuçları, hidrojen etkisinin kristal plastisite denklemlerine eklenmesine ve hidrojen gevrekleşme mekanizmasının daha detaylı anlaşılmasına önemli bir katkı sağlamaktadır.

Dedicated to my family and Dr. Canadinç...

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1 CHAPTER 1 INTRODUCTION

1.1 Motivation and Background

High-manganese (Mn) austenitic steels have stimulated significant attention owing to their concurrent high ductility, notable toughness, high strength and exceptional work hardening capacity, which make this class of steels a perfect candidate for load bearing applications for a variety of applications, especially in railroad and automotive industries [1]. The aforementioned optimum combination of mechanical properties of high-Mn steels are associated with coexistence of diverse micro-mechanisms, including dislocation slip [2,3], twinning [2-4], and phase transformation [5]. In addition to these primary mechanisms of plastic deformation, their interactions [3,6,7] and alloying elements [8,9] have been shown to significantly contribute to the exceptional work hardening capacity of this class of steels. The dominant one among these mechanisms, on the other hand, is dictated by several parameters, such as stacking fault energy (SFE), deformation temperature, and strain rate [10-14].

Previous works have demonstrated the distinctive role of SFE on the deformation behavior of high-Mn steels, such that the mechanical response is dominated by transformation-induced plasticity (TRIP), twinning-induced plasticity (TWIP), or dislocation glide only for the SFE values below 18-20 mJ/m², between 12 and 35 mJ/m², and above 35 mJ/m², respectively [10,15]. Specifically, lower SFE means lower energy barrier to facilitate abrupt orientation changes in the lattice, promoting martensitic transformation in TRIP steels, and mechanical twinning in TWIP steels [10,15]. The SFE itself is dictated by temperature and alloy composition. In particular, an increase in temperature increases the Gibbs free energy change required for any change in the lattice order, and hence, the SFE [16]. On the other hand, the effect of alloy composition depends on particular alloying elements: for

instance, the addition of Si decreases SFE, while that of Al decreases it [12,17,18]. However, Mn content has an unusual effect, such that Mn content up to a certain limit decreases the SFE, whereas further increase in Mn content increases the SFE [16]. Specifically, an increase in Mn content from 25 wt.% to 27 wt.% usually increases the SFE, while a further increase of Mn content to 28 wt.% decreases the SFE [16].

To add more to the complicated work hardening mechanism of high-Mn steels, the active micro-deformation mechanisms show a strong dependence on a number of parameters, including deformation temperature and strain rate [13]. The effects of these parameters have been subject to several studies exploring the mechanical behavior of high-Mn at the micro-scale featuring different deformation velocities, ranging from slow to very high velocity, and various loading modes, such as monotonic tensile and compressive [19-22], impact [5,23], fatigue [24,25], torsional [26], flying wheel tensile experiments [17]. However, to the best of the authors' knowledge, none of these works focused on twinning activity and detailed analysis of microstructure evolution of high-Mn steels at high strain rates that establishes both the temperature and chemical composition dependencies. In the current study, high-velocity tensile, compressive, impact loads were applied on three different types of high-Mn steels in order to observe the effect of chemical composition, temperature and deformation velocity on the complicated deformation response of high-Mn austenitic steels by promoting twinning over the various mechanisms.

The investigations of three high-Mn austenitic steels clearly demonstrate that chemical composition is one of the significant factors that dictates the deformation behavior of high-Mn austenitic steels. This clear consequence of the completed study prompted us to investigate the unusual strain hardening response of one kind of high-Mn austenitic steel, namely, Hadfield steel (HS). Hadfield steel exhibits high wear resistance combined with high ductility and strength, possesses an inherent toughness and an exceptional work hardening capability

[27-31]. These remarkable combination of the aforementioned mechanical properties have made HS the candidate material for various applications such as earthmoving, railroad and mining industries [32]. The lattice structure is face-centered cubic (fcc) at room temperature, mainly due to chemical stabilization of austenite by carbon (C) and manganese (Mn) in the microstructure [6], resulting in improved strain hardening behavior.

Previous works have demonstrated that twin boundaries, stacking faults and dynamic strain aging (DSA) due to the reorientation of carbon members of manganese-carbon couples are the main cause of rapid work hardening of HS [33]. Although DSA in several metallic alloys have been investigated deeply, the role of DSA in HS has not been carried out yet. The current study was undertaken with the motivation of improving the understanding of strain hardening mechanisms in HS by investigating the role of DSA closely. For this purpose, DSA was incorporated into the hardening algorithm of Visco-Plastic Self-Consistent (VPSC) code in order to observe negative strain rate sensitivity (NSRS) in HS.

The model which was used to compute DSA effect on overall hardening response of HS is based on multi-scale modeling approach. At atomistic level, the stress field imposed on the arrested dislocations due to carbon atom was modeled. Then effect of shear stress was implemented into crystal plasticity computations in micro-scale. Overall, our combined experimental and modeling effort provides an understanding for incorporating the DSA effect into crystal plasticity.

The multi-scale model was then further extended to estimate the hydrogen (H) effect on the mechanical behavior of the hydrogen storage materials. Despite the fact that the work focused on iron-based matrix since its microstructure is easy to analyze, the outcomes is applicable to all metallic storage materials to be utilized in hydrogen-fuelled applications. Hydrogen can easily diffuse into metallic materials and changes the mechanical properties of material at different scales. Hydrogen embrittlement (HE) which is a degradation mechanism

that leads to catastrophic failure for metallic materials exposed to H, is a very important factor affecting the safety, design procedure and maintenance of various applications, such as hydrogen storage, thermo-nuclear reactors, next generation automobiles, gas- and oil-pipelines, and renewable energy and fuel cells [34-37]. Although there are extensive number of studies about HE, the extant mechanism of HE is not obvious, yet a few mechanisms were proposed in the light of experiments, namely stress-induced hydride formation and cleavage, which is a result of formation of hydrides at stress concentration locations and volume dilatation [38-41], hydrogen-enhanced localized plasticity (HELP) which is the most widely used mechanism based on both experimental observations and theoretical calculations [42-44] and hydrogen induced decohesion which states presence of H in solid solution causes weakening for bonding at the crack tip accounting for the thermo dynamical analyses [43,45-47].

In the current study, HELP mechanism is preferred for the atomic-scale modeling. Despite the fact that H diffusing into a metallic material can serve as an effective barrier against dislocation motion and retard the glide of dislocations, leading to the pile-up effects and thereby local hardening in the matrix, hydrogen-containing metallic materials usually fail at stress levels that are lower as compared with their hydrogen-free counterparts. This can be explained with the HELP mechanism, such that the diffused H in host atom decreases the barriers to dislocation motion and causes the localization of slip bands, and thus, increases the dislocation mobility, which causes softening of the matrix material [42-44].

In order to analyze an exact mechanism of HE, experimental and numerical studies were carried out. In the experimental part, hydrogen free and hydrogen induced samples were deformed until fracture by tension loads. In the modeling part of this study, the calculation of hydrogen concentration was carried out firstly in order to observe hydrogen effect at atomic level. Then corresponding hydrogen effect was incorporated into the physically based crystal plasticity formulations. The modified visco-plastic self-consistent model successfully predicted the role of hydrogen interstitials on the macroscopic deformation response of iron polycrystals.

Finally, macroscopic deformation responses of our model were compared with the experimental results. As a result of our combined experimental and modeling effort, transient responses of solute diffusion and associated microstructural changes were investigated and corresponding mechanical response changes were modeled successfully and the mechanism of HE was understood more deeply.

1.2 Objectives

The current study aims to investigate the role of micro-deformation mechanisms on the performance of high strength steels. For this purpose, microstructure and deformation response of three different metallic materials were investigated under different type of loading scenarios experimentally. In addition to these experimental works, numerical studies were carried out in order to investigate the effects of hydrogen and carbon interstitials on deformation response of materials with the aid of multi scale modeling approach. These studies were also strengthened by comprehensive experiments. Finally, new multiscale modeling approach was proposed to predict the impact response of biomedical NbZr alloy by incorporating microstructural aspects.

Initially, the deformation responses of TWIP and XIP steels were investigated under high-velocity impact loading with a focus on micro-scale deformation mechanisms (Chapter 2.2). Although mechanical performances of TWIP and XIP steels have been studied under tensile or compressive loading, there is only a limited number of studies investigating the microstructure evolution of high-Mn steels under high-strain rate deformations, such as impact loading, which induces the micro-deformation mechanism interactions during deformation due to the complexity of the applied loading. With this motivation, the complicated deformation response of TWIP and XIP austenitic steels were investigated under

high velocity impact loading within a wide temperature range. Specifically, it has been demonstrated that twinning significantly contributes to the overall hardening of the high-Mn austenitic steels owing to the progressive nature of twin-slip interaction since twins form at the earlier stages of deformation and start to interact with glide dislocations as plastic deformation proceeds. The objective of this study was to observe the composition and temperature effects on the TWIP and XIP steels' deformation responses and microstructure under impact loading. Overall, the current findings demonstrate that the deformation of TWIP steel is dictated by two major twin systems at elevated temperatures, while nano-twin formation within one primary twin system dominates at low temperatures. The XIP steel, on the other hand, deforms mainly by slip at elevated temperatures, while competing slip and twin activities, and eventually nano-twin formation within primary twins prevail as the temperature decreases.

Following this study, high-velocity compression tests were carried out on three different types of high-manganese (Mn) austenitic steels, namely Hadfield, TWIP and XIP steels at three different temperatures (Chapter 2.3). The strain rate in this study was greater than the strain rate in the previous study. The focus of this work was induced enhanced twinning activity over slip at very high strain rates. For this purpose, a custom-made experimental setup was built. Specifically, it was observed that the nano-twin formation within the existing twins plays a crucial role on the deformation response of high-Mn austenitic steels.

Next, very high-tensile loads were applied on two different types of high-Mn steels utilizing a Split Hopkinson pressure bar setup (Chapter 2.4). The strain rate in this study was greater than the strain rate in the previous studies. The goal of this study was to observe the effect of chemical composition on the twinning behavior of high-Mn austenitic steels at different temperatures. Specifically, rare deformation mechanism of twinning-induced

plasticity (TWIP) steel was observed at room temperature, where ladder-like twinning was observed at both micro- and macro-levels. For the XIP steel with a higher Mn content, on the other hand, nano-twin formation within primary twins was prevalent, especially at low temperatures.

In the following part of current work, a new multi-scale modeling approach is proposed to predict the contributions of dynamic strain aging (DSA) and the resulting negative strain rate sensitivity (NSRS) on the unusual strain hardening response of Hadfield steel (Chapter 3). For this purpose, a crystal plasticity model was developed incorporating DSA into standard VPSC model, where the classical Voce type hardening was modified by taking into account the flow stress contribution that reflects the stress field imposed on the arrested dislocations due to rate dependent solute field surrounding them. The results then were compared to the experimental results obtained from strain rate jump tests on HS polycrystals. The simulation results demonstrated the success of the proposed model in predicting the role of DSA on the mechanical response of the HS, including the NSRS exhibited by this material.

Finally, the hydrogen effect on the mechanical behavior of the iron was experimentally investigated and numerically modeled at low strain rates in order to improve the understanding of hydrogen embrittlement (Chapter 4). Based on experiment results, classical Voce hardening scheme was modified to account for the shear stresses imposed on arrested dislocations due to the surrounding hydrogen interstitials. This study presents a physically based crystal plasticity formulations, which were successfully applied to iron matrices. The modified visco-plastic self-consistent model successfully predicted the role of hydrogen interstitials on the macroscopic deformation response of iron polycrystal. As a result of our combined experimental and modeling effort, transient responses of solute diffusion and

associated microstructural changes were investigated and corresponding mechanical response changes were modeled successfully.

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2 CHAPTER 2 RESEARCH RELATED TO HIGH MANGANESE ALLOYS

2.1 Introduction

2.1.1 Motivation and Background

A significant fraction of research efforts aiming at improving the mechanical performance of light-weight metallic materials have focused on magnesium (Mg) and aluminum (Al) alloys [1–5]. However, recent developments in the field of advanced high-strength steels have opened the venue for utilizing steel components with reduced weight without sacrificing from strength and ductility. Consequently, various new generation steels, especially high-manganese (Mn) austenitic steels, have become an alternative to Mg- and Al-alloys, and are now utilized in different types of modern engineering applications, such as in the automotive, railroad and mining industries [6–9]. However, this class of steels features complex microstructural interactions during deformation, which makes the mechanical properties and deformation behavior difficult to predict for any given initial texture and microstructure. Hence, high-Mn austenitic steels have been subject to numerous works.

Earlier studies on high-Mn austenitic steels focused mainly on Hadfield steel, a type of austenitic high-Mn steel with 1-1.4 wt. % C and 10-14 wt. % Mn, which possesses a stable austenitic microstructure with a face-centered cubic (fcc) lattice, offering a good combination of high strength and significant ductility, in addition to high wear and abrasion resistance [10–17]. One of the important conclusions drawn from these previous works was that low stacking fault energy (SFE) resulting from the high-Mn content promotes formation of twins. Specifically, as the SFE decreases, the level of energy required for the abrupt lattice rotation associated with mechanical twinning also decreases, eventually enhancing twin formation, which provides effective barriers against dislocation glide, and leads to significant strain

hardening [18]. On the other hand, the SFE increases upon alloying with elements, such as Al and Si, favoring slip-dominated plastic deformation while decreasing the contribution of twins and stacking faults to the overall hardening [12,19]. However, even in the case of high SFE, interaction between dislocations and different features of the microstructure, such as dense dislocation walls, promotes rapid strain hardening in this class of steels [12,20].

In addition to SFE, deformation temperature and dynamic strain aging (DSA) also have significant influence on the work hardening behavior of high-Mn steels. First of all, deformation becomes slip-dominant with the increase in temperature [21], and thus, due to hindered interaction with twins and twin boundaries, work hardening capacity of the material decreases. Furthermore, interactions between C atoms in the C-Mn clusters and dislocations, and reorientation of C atoms in dislocation cores lead to DSA, and improve the work hardening capacity of Hadfield steel by hindering the dislocation motion [22,23].

All these findings on Hadfield steel and further research led to the introduction of relatively higher Mn containing (13-30 wt. % Mn) steels, and eventually the development of TWIP (TWinning Induced Plasticity) steels [24–29]. This class of steels possess an excellent combination of high strength and ductility: typically, strengths (UTS) up to 1500 MPa, elongations up to 90%, and outstanding impact toughness ranging from 90 to 120 J/cm² at high strain rates have been reported for TWIP steels at various temperatures [24–29]. In addition to these superior mechanical properties, TWIP steels possess relatively lower density ($\rho \approx 7.3 \text{ g/cm}^3$) and much higher energy-absorption capacity (0.5 J/mm³) than conventional steels, with typical density and energy absorption values of 7.8 g/cm³ and 0.25 J/mm³, respectively [27–31].

Many of the previous investigations reported that twinning accompanied by additional micro-mechanisms, such as stacking faults, DSA and slip-twin interactions, dominates the deformation response of TWIP steels, where the role of dislocation glide remains rather

limited in comparison [32–35]. In particular, at the onset of plastic deformation, twins start to nucleate and the amount of nano- and micro-scale twins increase during plastic deformation, forming twin boundaries of different magnitudes. In materials that are only deformed by dislocation glide, the mean free path of dislocations is a function of grain boundary (GB) density and dislocation-dislocation interactions. However, in the case of TWIP steels the twin boundaries formed within the microstructure also play a crucial role. Specifically, the mean free path of dislocations is reduced by increasing twin boundaries, which act as strong obstacles against dislocation glide and bring about the noticeable strain hardening observed in TWIP steels [19,32,33,36]. This is known as the TWIP effect, which is triggered at low or medium SFE values ($12\text{--}35\text{ mJ/m}^2$) [37]. Both, the TWIP effect and microstructural interactions suspend the onset of necking since they are obstacles for dislocation glide, and as a result, high ultimate tensile strength values with extraordinary ductility is achieved before necking in high-manganese austenitic TWIP steels [27,29,38–40]. However, if the mobile dislocation density is not large enough or the mean free path of dislocations is not short enough to provide for the critical twin nucleation stress, growth of existing twins is favored over the nucleation of new ones. As a result, the volume for microstructural interactions becomes smaller, and therefore, easier dislocation glide takes place, eventually leading to softening of the material [41].

The aforementioned superior mechanical performance of TWIP steel has been observed in various investigations, which focused on tensile properties [8,38,39,42,43], deformation behavior and the corresponding micro mechanisms [29,40,44–46], fatigue [27,47–52], effects of alloying elements [31,53–56] and fracture [56,57] of high-Mn TWIP steels. Consequently, it was reported that TWIP steels have high strain hardening capacity due to twin-slip interactions under tensile or compressive loading. However, there is only a limited number of studies investigating the microstructure evolution of high-Mn steels under

high- and very high-strain rate deformations which induces the micro-deformation mechanism interactions during deformation due to the complexity of the applied loading [6,58]. Even though Wen et al. [6] and Toker et al. [58] reported the deformation behavior of a new generation high-Mn austenitic steel under impact loading, to the best of authors' knowledge, a detailed analysis of microstructure evolution of high-Mn steels under high- and very high-strain rate loading that establishes both the temperature and chemical composition dependencies has not been carried out yet.

As opposed to static, quasi-static or cyclic tensile/compressive loading, high- and very high-strain rate loading enhances only one deformation mechanism rather than their complex interactions, which enables a more comprehensive and straightforward understanding of the microstructural evolution of high-Mn steels [58]. In the present study, microstructural aspects of the high work hardening capacity of high-Mn steels with different chemical compositions were investigated with the aid of high strain rate experiments. Also, contribution of nano-twin formation within the existing twins to overall strain hardening response of these steels were investigated. The loading conditions, such as deformation temperature and velocity, and the material's chemical composition, play a crucial role for the determination of the dominant deformation mechanism and the corresponding deformation response. In order to explore the role of temperature, which dictates the deformation mechanism parameters, such as the twin volume fraction, twin thickness and glide dislocation density, three different testing temperatures were chosen to represent a wide temperature range of -170 °C to 200 °C. The microstructure and deformation mechanisms of the as-is and deformed materials were investigated by optical microscopy, stereographic microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The current set of experiments have opened a venue to investigate the complicated deformation response of high-Mn austenitic steels by promoting twinning over the various

mechanisms with the application of high velocity loading within a wide temperature range. Specifically, it has been demonstrated that twinning significantly contributes to the overall hardening of the high-Mn austenitic steels owing to the progressive nature of twin-slip interaction since twins form at the earlier stages of deformation and start to interact with glide dislocations as plastic deformation proceeds [58]. In addition to these interactions, nucleation of new twins and a larger volume fraction of slip-twin interactions are promoted by slip that further distorts the lattice [41]. The investigation of high-Mn austenitic steels with different chemical compositions, on the other hand, allowed for the investigation of the role of alloying elements on the aforementioned interactions. Overall, the current findings demonstrate that the deformation of TWIP steel is dictated by two major twin systems at elevated temperatures, while nano-twin formation within one primary twin system dominates at low temperatures. The XIP steel, also commercially named as X-IP™ 1000 (provided by Arcelor Mittal), on the other hand, deforms mainly by slip at elevated temperatures, while competing slip and twin activities, and eventually nano-twin formation within primary twins prevail as the temperature decreases. Moreover, formation on nano-twins within existing twins in high-Mn steels improves the work hardening capacities. Furthermore, the current results clearly lay out the effects of temperature and chemical composition on the twinning response of high-Mn austenitic steels under high strain rate loading and lead to the utilization of this class of alloys in applications bearing high-velocity loading. The conducted high strain rate experiments, which are in the order of impact test, high strain rate compression test and Split Hopkinson test, and corresponding results and discussions are presented in the upcoming subsections.

2.2 On the Micro-Deformation Mechanisms Active in High-Manganese Austenitic Steels Under Impact Loading

2.2.1 Experimental Details

Two different grades of high-manganese austenitic steels, namely a TWIP steel and an XIP steel, were studied. Table 2.2. 1 presents the chemical compositions of these two steels. Surfaces of the TWIP and XIP steel samples were prepared by standard grinding and polishing metallographic equipment, and etched with a solution of 5% nitric acid in methanol for approximately 1 minute, and then cleaned with ethanol. Following the metallographic preparations, microhardness values (HV0.1) of all TWIP and XIP samples around the notch were examined using a micro-hardness tester. Line measurements with a spacing of 0.09 mm between the indents were conducted on both sides of the notch as this is the critical region for impact deformation. The average Vickers hardness values for the undeformed TWIP and XIP steels were found as 280 and 330 HV, respectively, and the hardness values were observed to be near-uniform around the notch, which demonstrated the near-uniform microstructure of the as-is samples.

Table 2.2. 1 Chemical compositions of TWIP and XIP steels (wt. %) [59].

Steel	C	Si	Mn	Ni	Cr	V	Co	Ti	Fe
TWIP	0.628	2.601	14.843	0.065	0.043	0.023	0.013	0.006	Balance
XIP	0.600	0.190	20.990	0.018	0.118	0.129	0.011	0.005	Balance

For monitoring the impact response of the materials, Charpy-V shaped TWIP samples with dimensions of 55 mm × 10 mm × 2 mm, and XIP samples with dimensions of 50 mm × 10 mm × 2 mm were cut utilizing electro-discharge machining¹. All impact samples featured a 45° notch with a radius of 0.25 mm and a depth of 2 mm, and were subjected to an impact energy of 150 J, which corresponds to an impact velocity of 5.5 m/s. The experiments were conducted at -170 °C, room temperature (RT) and 200 °C. Liquid nitrogen and furnace heating were utilized for cooling down and heating up of the samples, respectively.

The impact energies of XIP and TWIP steels at each temperature were measured as provided in Figure 2.2. 1, indicating that the ductile-to-brittle transition temperatures were below RT. Moreover, there is a slight decrease in impact energy values when the temperature changes from RT to 200 °C, such that the increased number of active micro-deformation mechanisms at RT provides more means of dissipating energy, increasing the impact energy absorption capacity of both the TWIP and XIP steels, as detailed in the following section. The observed ductile-to-brittle transition behavior enables the investigation of micro-deformation mechanisms leading to both ductile and brittle fracture since the test temperatures (-170 °C, RT, 200 °C) were chosen with the purpose of covering both the low temperature brittle response and the high temperature ductile behavior, as well as the transition range. One can argue that, based on the data presented in Figure 2.2. 1, RT does not fully cover the transition range, however; the changes in micro-deformation mechanisms demonstrate the beginning of transition, as evidenced by the results of the thorough TEM analysis (Table 2.2. 2).

The temperature changes at the instant of impact and during fracture were detected by a thermal camera operated in-situ. The optical microscopy and stereographic microscopy were carried out to examine the surface microstructure prior to and following the experiments, where the latter provides a more detailed three-dimensional image of the sample surface.

¹ This slight difference in sample dimensions stems from the geometry of the XIP steel initially available.

SEM and TEM observations were performed in order to obtain more information about the TWIP effect and the states of micro-deformation mechanisms under impact loading. For TEM work, thin foils in form of flat disks were extracted from the notch tip of each tested sample, such that the surface normal of a disk foil coincided with the impact direction and the corresponding disk thickness was approximately 250 μm . These disks were then mechanically thinned down to 80 μm , and in order to obtain large electron-transparent areas, electropolished on both sides by conventional twin-jet electropolishing with an electrolyte consisting of 100 ml 40 % perchloric acid, 500 ml butoxyethanol and 400 ml acetic acid. The electropolishing was carried out at -20 °C under an acceleration voltage of 20.5 V.

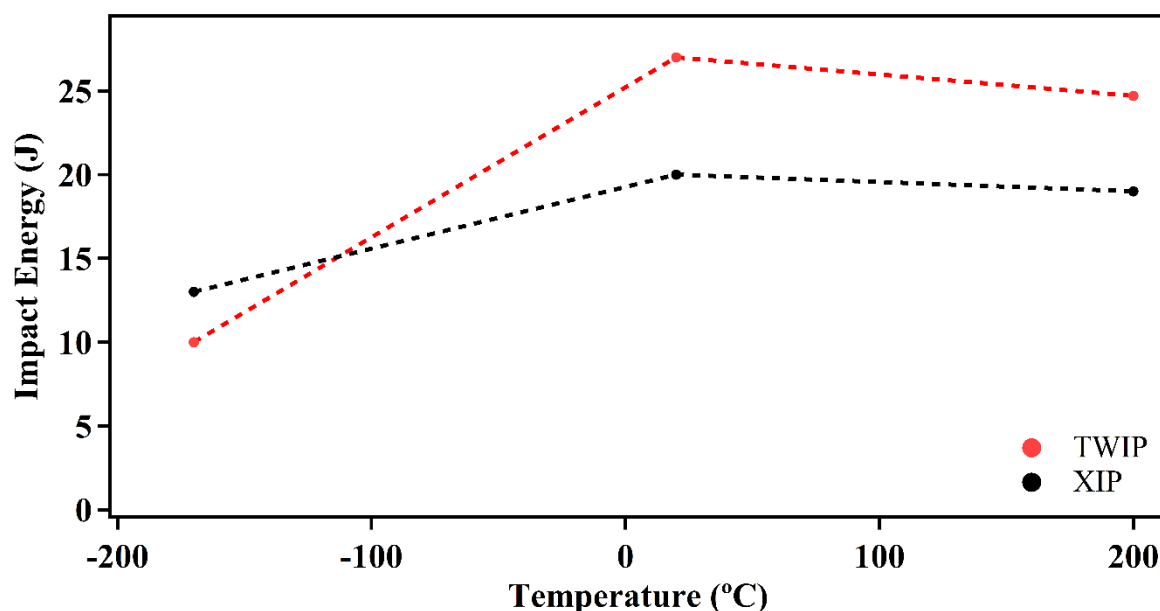


Figure 2.2. 1 Impact energy vs. temperature plot for the XIP and TWIP steels [59].

Table 2.2. 2 Deformation mechanisms observed at all temperatures for the TWIP and XIP steels [59].

	200 °C	RT	-170 °C
TWIP	2 T, S, V	TT, S, V	TT, S, V
XIP	S	2 T, S, V	TT, S
<i>S: slip</i>	<i>T: twin</i>	<i>TT: twin-inside-twin</i>	<i>V: void formation</i>

2.2.2 Results and Discussion

2.2.2.1 Microstructural Investigation

The active micro deformation mechanisms observed in both materials at each test temperature are tabulated in Table 2.2. 2. The investigations on the lower Mn-containing sample, i.e. the TWIP steel, have demonstrated the coexistence of slip, twin, and voids at 200 °C as illustrated in Figure 2.2. 2. The two twin variants observed throughout the microstructure are highlighted in Figure 2.2. 2 (a). In addition to twinning, dense dislocations (Figure 2.2. 2 (a)) and voids (Figure 2.2. 2 (b)) are visible at elevated temperatures. This deformation response dictated by two active twin systems was also previously observed, where high velocity ballistic impact tests were carried out at RT [44]. The significant increase of temperature stemming from the high-speed impact load during ballistic penetration causes the steel to deform via the same mechanisms, i.e. twinning with two variants and dense dislocations interacting with these twins [44], as in conventional impact test at elevated temperatures which was utilized in this study. However, as temperature decreased down to RT (Figure 2.2. 3 (a)), and then to -170 °C (Figure 2.2. 3 (b)), secondary nano-twins were observed to form within the primary twins instead of different twin variants. The nano-twin formation in TWIP steel at RT was not reported in studies where conventional low velocity

uniaxial tension [34] and high-pressure torsion experiments [60] were performed. In the former, only a secondary twin system in addition to the primary twins was activated with increasing amount of strain [34]. For the latter, instead of nano-twin formation, secondary and tertiary twin systems were shown to be triggered for two and three torsional cycles, respectively [60]. In addition to the change in twinning behavior, as deformation temperature decreased down to RT (Figure 2.2. 3 (a)) then to $-170\text{ }^{\circ}\text{C}$ (Figure 2.2. 3 (b)), dislocation activity also decreased as only a low density of dislocations was observed and dislocation-twin interactions were scarce.

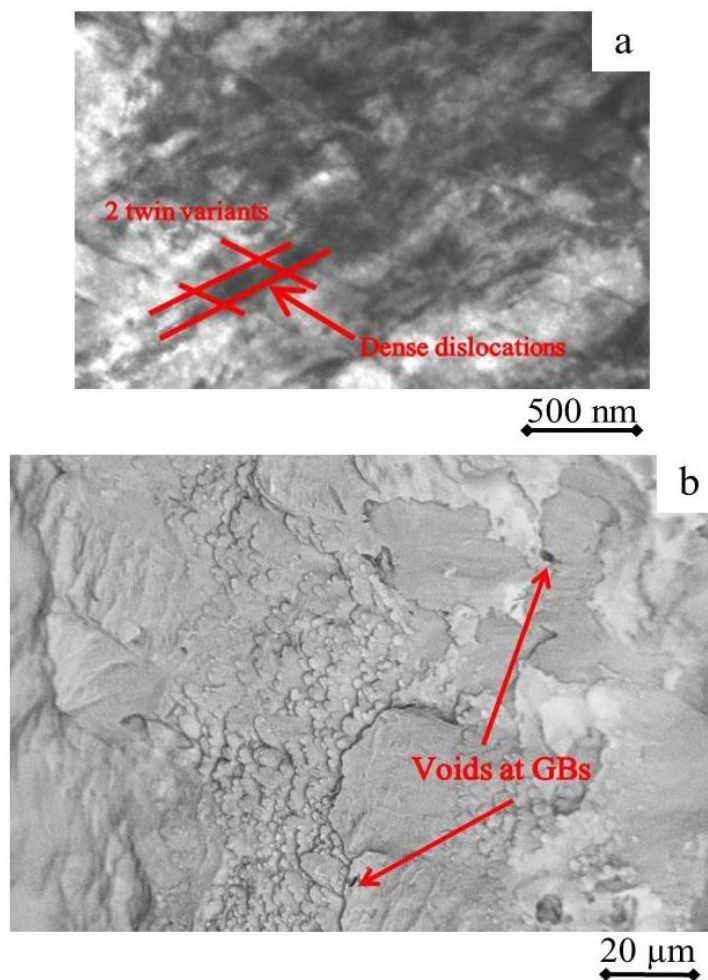


Figure 2.2. 2 (a) The two twin variants integrated with dense dislocations and (b) voids formed at GBs for TWIP steel deformed at $200\text{ }^{\circ}\text{C}$ [59].

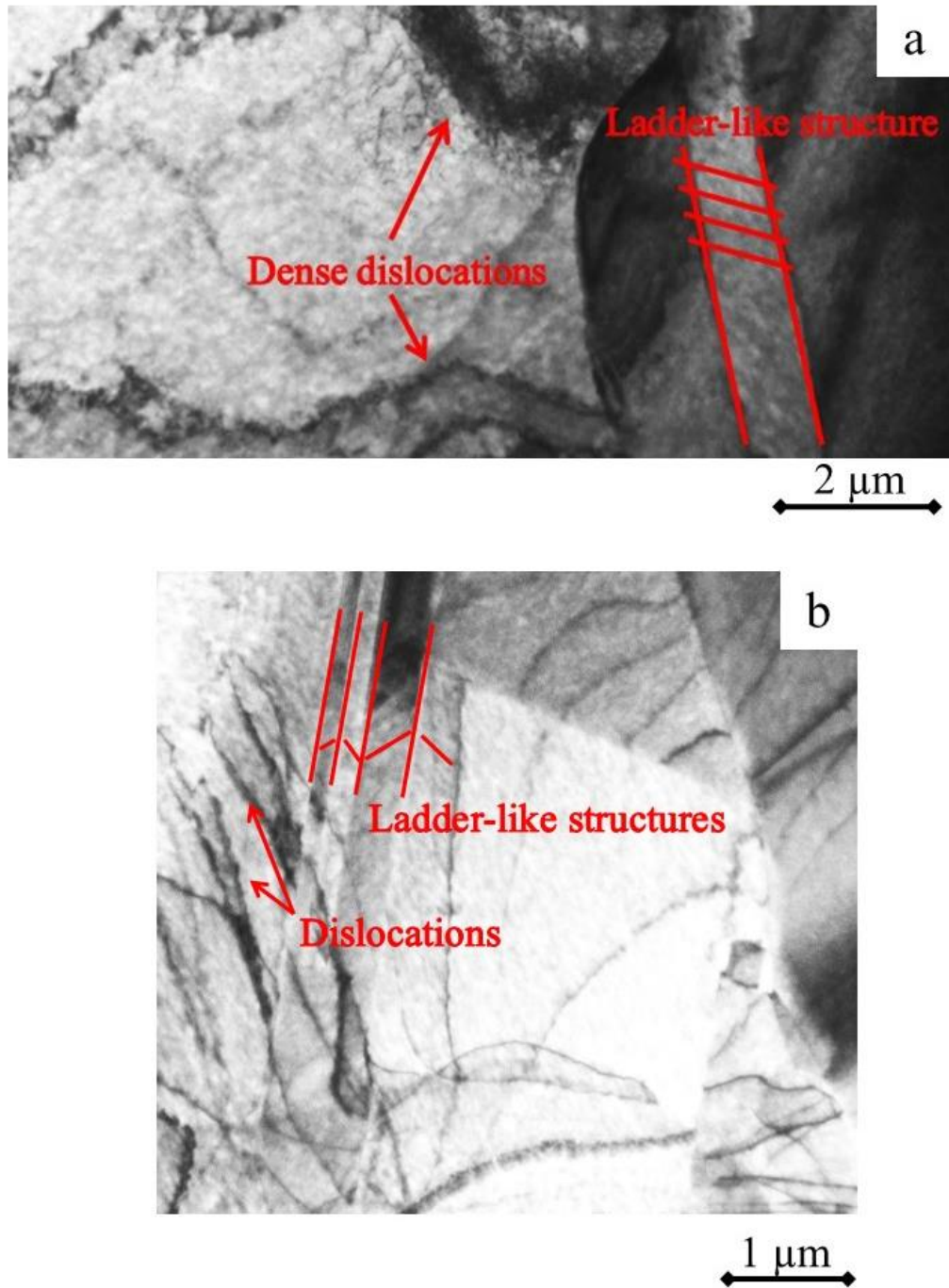


Figure 2.2. 3 Microstructure of TWIP steel following deformation at (a) e RT and (b) -170 °C: nano-twins inside primary twins forming ladder-like structures and dense dislocations are visible [59].

For the XIP steel, on the other hand, the dominant deformation mechanism dictating the deformation was slip at elevated temperatures (Figure 2.2. 4) due to the higher content of Mn, which increases the SFE: This increase in SFE increases the threshold energy required

for abrupt orientation evolution during twin nucleation, such that the resulting twinning can only form at low temperatures (Figures 2.2. 5 and 2.2. 6). As temperature decreased, slip activity became less significant, such that the material deformed by both twinning and slip at lower temperatures. In addition to the change in deformation response with decreasing temperature, the twinning scenario also changed from two different twin variants forming at RT (Figure 2.2. 5 (a)) to nano-twin formation within primary twins at -170 °C (Figure 2.2. 6). The decrease in diffusion was also realized by an increased deformation rate in a study where tension tests were carried out at velocities of up to 20 m/s [8]. The increased deformation speed also resulted in a decrease in dislocation activity and enhanced twin formation which increased the overall strength of the material [8]. By a decrease in temperature down to RT, two different twin variants were observed in addition to slip lines (Figure 2.2. 5 (a)). The number of active twin variants and their interactions with glide dislocations agree well with the findings of previous works, where room temperature uniaxial tension tests [47,61,62] and split-Hopkinson bar (SHB) tensile tests [28] were carried out on steels with a Mn content close to that of the XIP steel. However, the twin activity was detected to be increased in the current work with respect to standard uniaxial tension tests [47,61,62] related to the high deformation velocity during the impact test. However, the dislocation activity was similar in the study in which high velocity SHB tension testing was utilized [28]. The decrease in dislocation activity was also demonstrated in a study where isothermal compressive load was applied to XIP steel [63]. The deformation response was changed from only slip to two different twin variants with integrated dislocation substructures [63]. This enhanced twinning due to a temperature decrease was previously reported for tension tests conducted at RT and in liquid nitrogen [26], where the twin density over dislocation density was observed to increase with decreasing temperature. The decrease in dislocation density observed in the current study is attributed to the high-velocity deformation, which limits dislocation motion

within the microstructure. In addition to twins, voids were detected only at RT (Figure 2.2. 5 (b)). Further decrease in temperature to -170 °C caused nano-twins to form within previously formed twins (Figure 2.2. 6). This nano-twin formation was also observed in the work by Timokhina et al. [64], where severe plastic deformation was applied via equal angular channel pressing at high temperatures. The high temperature during loading resulted in enhanced dislocation slip [64], which is not the case in this study.

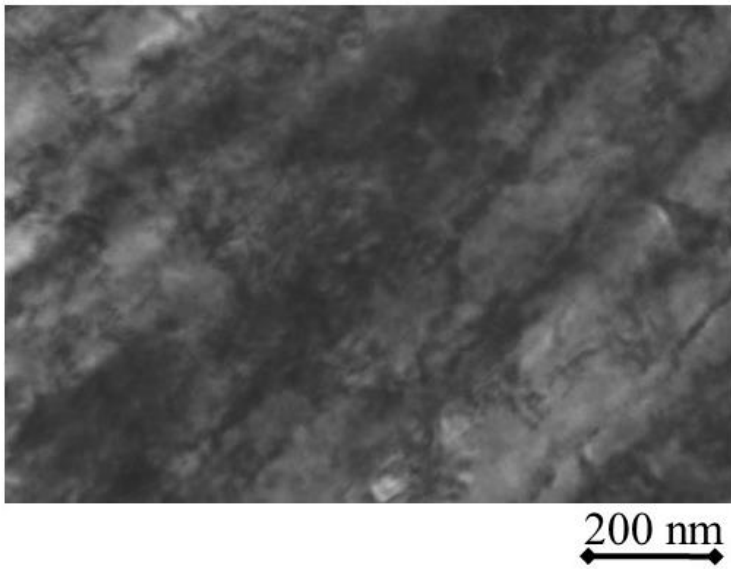


Figure 2.2. 4 Microstructure of XIP steel deformed at 200 °C: dislocation slip dominates the microstructure [59].

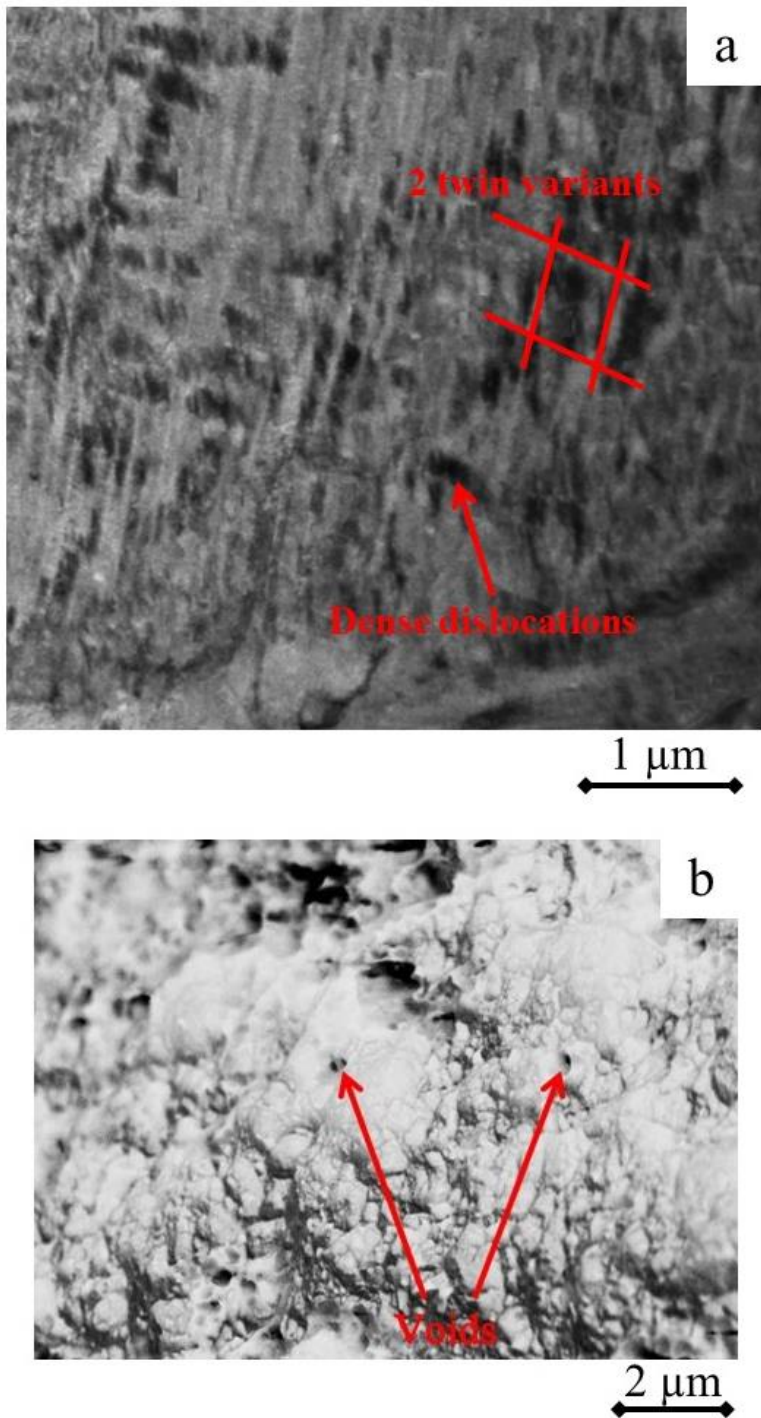


Figure 2.2. 5 Microstructure of XIP steel deformed at RT: (a) Two different twin variants and dense dislocation structures within twins and (b) voids formed during deformation [59].

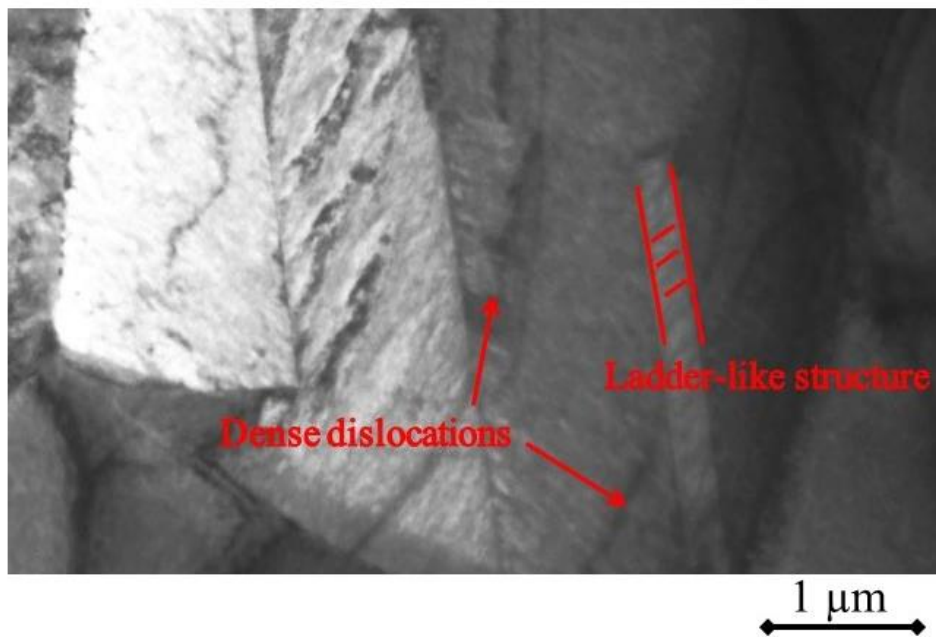


Figure 2.2. 6 Dense dislocations and nano-twins that formed in XIP steel sample upon deformed at -170 °C [59].

2.2.2.2 Thermographical Analyses

The deformation of both steels at 200 °C and RT were recorded by a thermal camera in order to detect sudden temperature increases at the moment of impact. The sensitivity of the thermal camera utilized in the current study was less than 0.02 °C, such that the accuracy of the measurements were within the ± 1 °C for temperatures up to 150 °C and ± 2 °C for higher temperatures. The results of the analyses at 200 °C and RT are presented in Figures 2.2. 7 and 2.2. 8, respectively. The ductile and more brittle fracture behaviors of XIP and TWIP steels were evident from the temperature distribution within the fracture zone during impact. At 200 °C, the temperature increase in XIP was higher than that of TWIP, i.e. about 60 °C vs. about 20 °C. This phenomenon stems from the lack of micro deformation mechanisms activated at high temperatures in XIP steel as it deforms only by dislocation slip. Therefore, the given energy through impact loading could not be transferred into lattice distortion, instead it is mostly transformed into heat. On the other hand, TWIP steel deforms by various micro mechanisms in addition to dislocation slip, such as twins and to a small

amount by formation of voids, which decrease the amount of energy dissipated through heating of the sample. Hence, the temperature increase is smaller for the TWIP steel. For the RT case, since both twinning and slip were activated both for the TWIP and XIP steels, the increase in temperature of the sample during deformation were 80 and 65 °C, respectively.

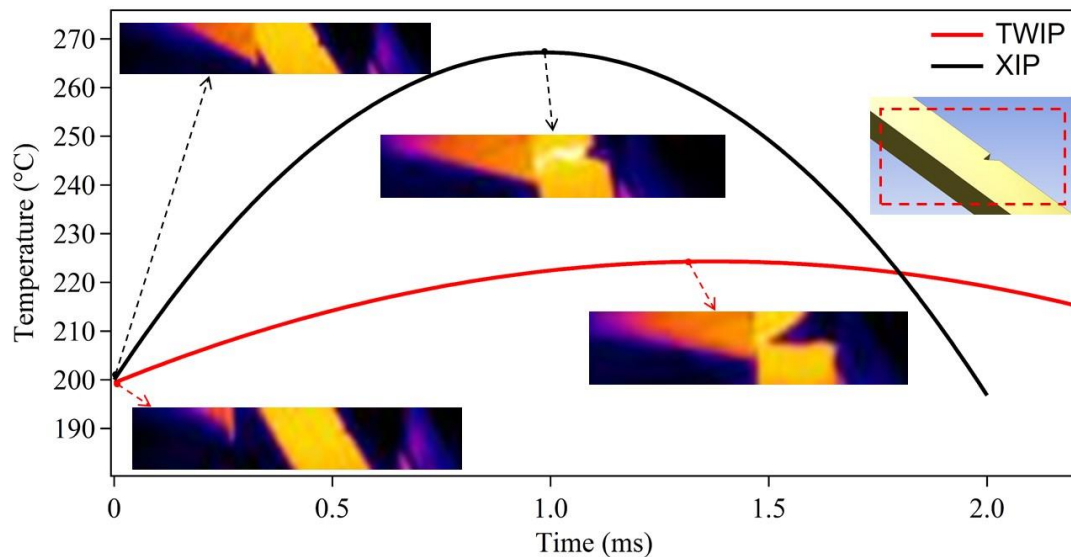


Figure 2.2. 7 In-situ thermal analyses of impact deformation of TWIP and XIP steels at 200 °C. The inset indicates which location on the samples the thermographs correspond to [59].

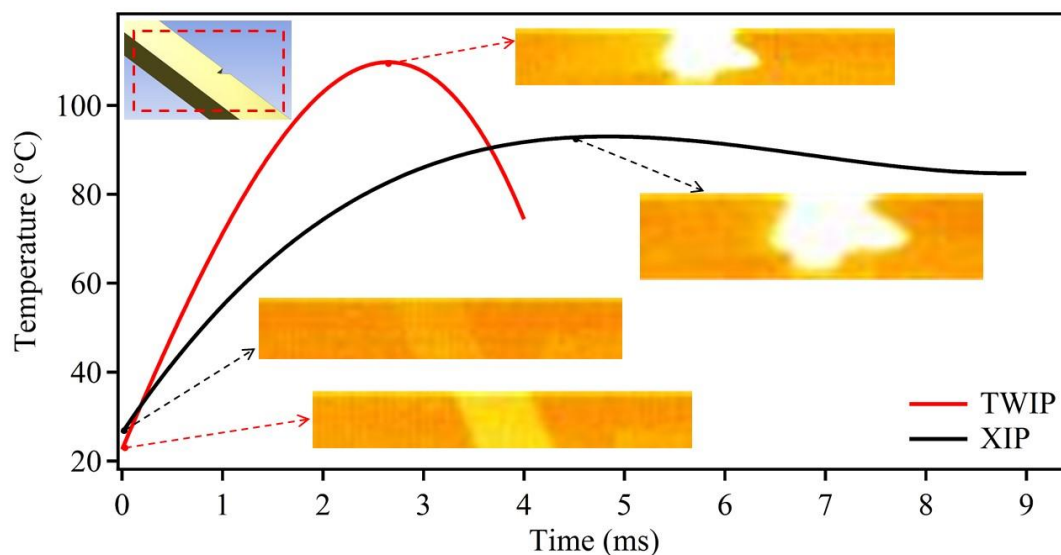


Figure 2.2. 8 In-situ thermal analyses of impact deformation of TWIP and XIP steels at RT. The inset indicates which location on the samples the thermographs correspond to [59].

2.2.3 Conclusions

A thorough microstructural investigation was carried out on two different classes of high-manganese austenitic steels with different alloying elements, namely TWIP and XIP steels, deformed under impact loading. Scanning electron microscopy and transmission electron microscopy were carried out on both undeformed and deformed samples, in addition to in-situ thermographical analyses that accompanied the impact experiments. The current set of results have shown that the dominating micro deformation mechanisms in TWIP and XIP steels differed at the same temperature, indicating the dependence of the deformation response on the chemical composition. Moreover, the deformation response was also dictated by the temperature, such that TWIP steel deforms by activation of two major twin systems at elevated temperatures, while nano-twin formation within one primary twin system dominates at subzero temperatures. The XIP steel, on the other hand, deforms mainly by slip at elevated temperatures, while competing slip and twin activities, and eventually nano-twin formation within primary twins dominate as the temperature decreases. In addition to microstructural investigation, the in-situ thermographical analyses during plastic deformation revealed the change in deformation response from a thermal perspective, such that when both twinning and slip were activated, the increase in temperature was lower as compared to the case where only slip prevailed. This relatively lower increase in temperature is an indication of the larger amount of energy dissipated to activate multiple mechanisms within the lattice. Consequently, the current findings shed light on the roles of individual mechanisms on the strain hardening behavior of high-manganese austenitic steels.

2.3 Investigation of Twinning Activities in High-Mn Austenitic Steels Under High-Velocity Compressive Loading

2.3.1 Experimental Details

The materials investigated in this study were Hadfield, TWIP and XIP steels. The chemical compositions of these materials are shown in Table 2.3. 1. After grinding and polishing procedures, the specimens were chemically etched with a solution of 5% nitric acid in methanol for approximately 1 minute, and then cleaned with ethanol. Surface microstructure investigations were conducted with the aid of optical and stereographic microscopies. TWIP effect and the states of micro-deformation mechanisms under high-velocity compression experiments were monitored by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) after the experiments.

Table 2.3 1 Chemical compositions of Hadfield, TWIP and XIP steels used in this study (wt. %) [65].

Steel	C	Si	Mn	Ni	Cr	V	Co	Ti	Fe
HS	1.090	0.432	12.340	0.148	0.297	0.035	0.044	0.007	Balance
TWIP	0.628	2.601	14.843	0.065	0.043	0.023	0.012	0.006	Balance
XIP	0.600	0.190	20.990	0.018	0.118	0.129	0.011	0.004	Balance

SEM analyses were performed on a field emission scanning electron microscope while a TEM equipped with a 200 kV electron gun was utilized for the TEM analysis. Extracted flat disks with a thickness of nearly 250 μm were used for TEM analyses. Then, electropolishing was conducted to these disks, which was thinned down to 80 μm , at -20 $^{\circ}\text{C}$ under an acceleration voltage of 20.5 V to achieve large electron-transparent areas.

The high-velocity compression tests were conducted using man-made experimental setup equipped with 3-kg hammer and thermographical camera (Figure 2.3. 1). The compression test samples with dimensions of 4 mm × 4 mm × 10 mm were extracted by electro-discharge machining. In order to establish the velocity dependence of compression test response of Hadfield steel, three different hammer falling height levels were adjusted: 2, 2.75, and 3.5 meters from the sample tray, which correspond to velocities in the range of 6-8 m/s. On the other hand, for TWIP and XIP falling height level steels was decided to be 0.5 meters, which is close to 3 m/s as deformation velocity. Falling height level greater than 0.5 m causes surface damage for TWIP and XIP samples. Moreover, in order to investigate temperature effect on deformation response, all tests were conducted at three different temperatures: -170 °C, RT, and 200 °C. The temperature changes at the instant of compression and during fracture were detected by a thermal camera operated in-situ.

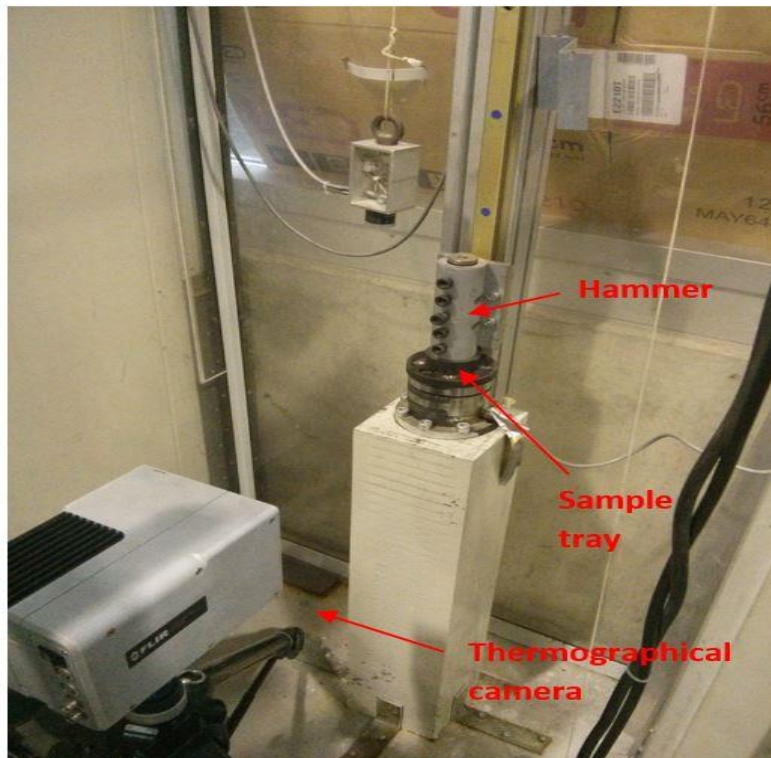


Figure 2.3. 1 The man-made experimental setup used in the high-velocity compression experiments [65].

2.3.2 Results and Discussion

Table 2.3. 2 demonstrates the active deformation mechanisms in the studied materials at different temperatures. All types of deformation mechanisms, i.e. slip, twin, twin-inside-twin, slip-inside-twin and voids, were observed in Hadfield steel, which has the lowest Mn content at all testing temperatures, as illustrated in Figure 2.3 2. Earlier investigations on Hadfield single crystals also revealed that two dominant twin systems and dislocation glide were activated by tensile [66] and compressive [67] loading. Moreover, it was also shown that two active twin systems dominate the high strain rate deformations in high-pressure torsion experiments [60].

Table 2.3 2 Active deformation mechanisms in the current materials at different temperatures [65].

	200 °C	RT	-170 °C
HS	S, ST ,T , V, TT	S, ST ,T , V, TT	S, ST ,T , V, TT
TWIP	2 T, S	TT, S	TT, S
XIP	S	3 T, TT, S	2 T, S
S: slip	T: twin	TT: twin-inside-twin ST: slip-inside-twin V: void	

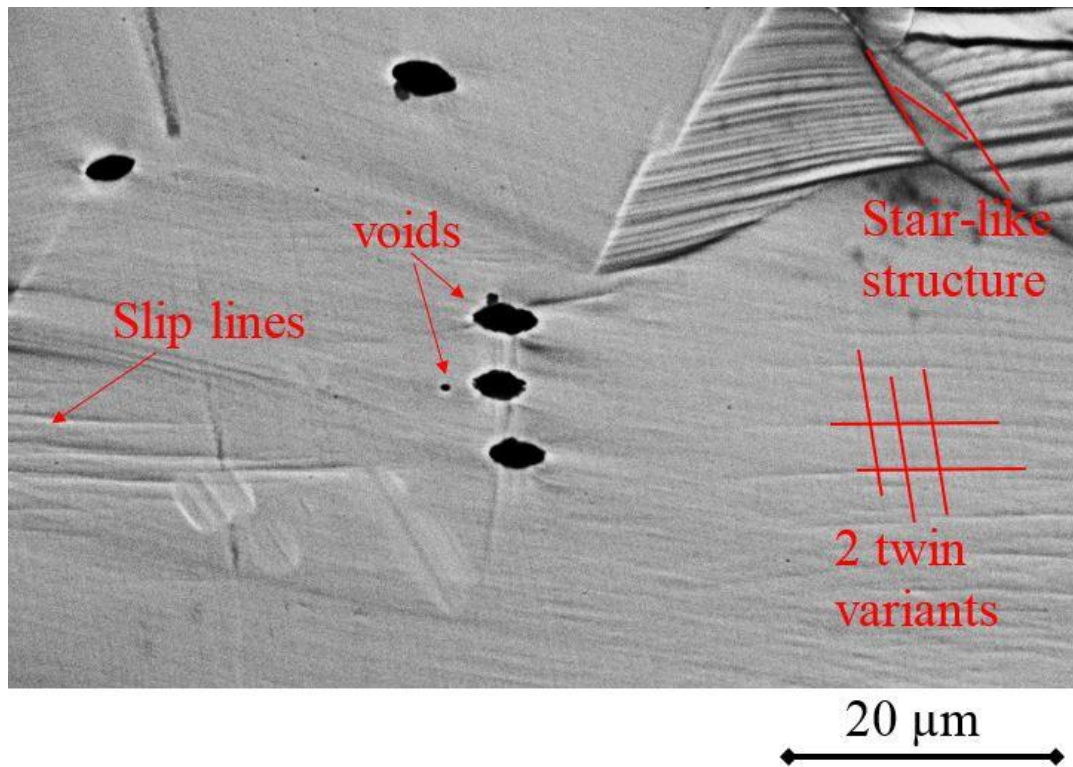


Figure 2.3. 2 SEM photomicrograph of Hadfield steel deformed at RT [65].

It was also observed that the mean free distance between dislocations gliding on the parallel system changes when the glide dislocations interact with the twin boundaries (Figure 2.3. 3). The results of Shen et al. confirm such change with a detailed study [68]: when a glide dislocation passes through a twin boundary, it dissociates into its partials which may cause the mean free distance change [68]. Thus, the decrease in the mean free distance of dislocations and increases in the energy barrier to be exceeded by dislocations are the results of secondary micro-twin formation.

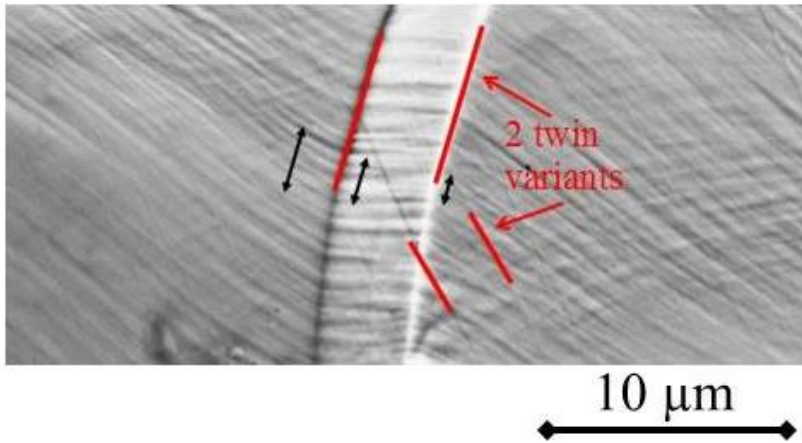


Figure 2.3. 3 Change in the width of slip line crossing a twin boundary [65].

As a result of enhanced twinning activity at $-170\text{ }^{\circ}\text{C}$, fracture mode was moved ductile to brittle which is shown in Figure 2.3. 4. This result stands in good agreement with the previous study on Hadfield steel, which was conducted at low temperature and similar deformation velocities with our experiments [58]. In this particular work, the material exhibited a ductile-to-brittle transition between -100 and $50\text{ }^{\circ}\text{C}$, and a ductile-to-brittle transition temperature between -50 and $0\text{ }^{\circ}\text{C}$ [58], which implies that the twinning activity is enhanced at low temperatures that promote low SFE, such that enhanced slip-twin interactions lead to brittle fracture. This result was strengthened with the optical microscopy images, which were taken to observe surface relief (Figure 2.3. 5). It is obvious from the figure that, brittle deformation behavior was observed due to enhanced twinning activity and slip-twin interactions.

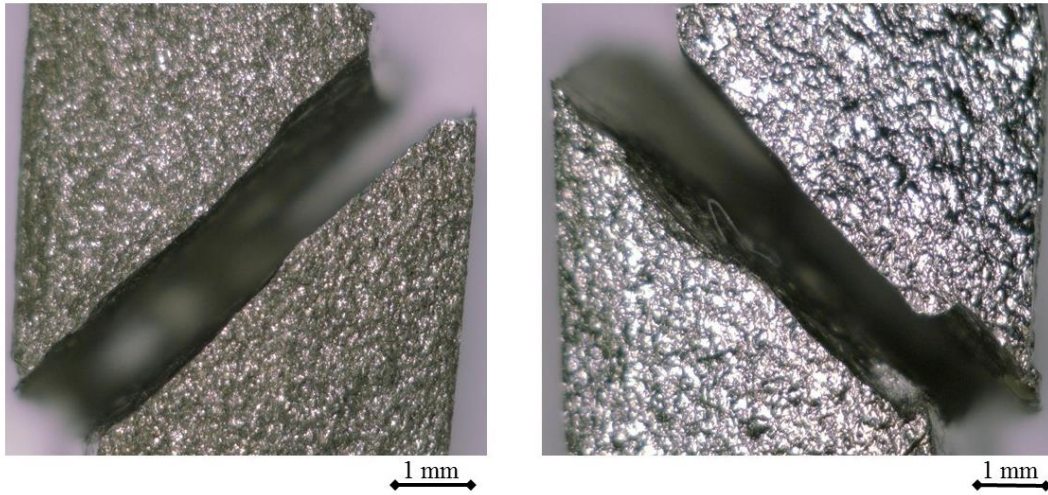


Figure 2.3. 4 Stereographic image of the fracture surface of the Hadfield steel at -170 °C [65].

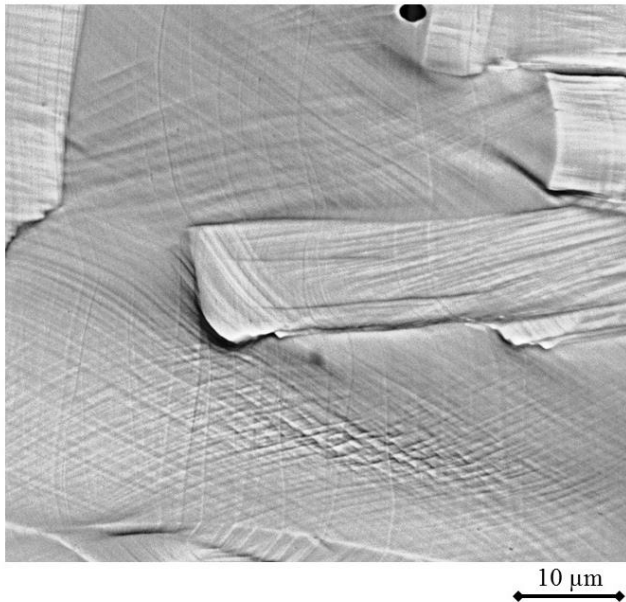


Figure 2.3. 5 Optical image of twin-slip interaction in Hadfield steel deformed at -170 °C [65].

Various types of twinning activity were observed at different test temperatures. For instance, activation of two different twin variants were detected at 200 °C (Figure 2.3. 6) and nano-twin formation inside a formed twin was observed at RT (Figure 2.3. 7(a)). The latter result stands in good agreement with the previous experiments which were conducted at high

temperatures [64]. Since TWIP steel has low SFE, nano-twin formation is observed even at high temperatures which induce dislocation glide rather than twinning.. However, dramatic temperature decrease diminishes the dislocation motion by decreasing the atomic diffusion and the SFE (Figure 2.3. 7(b)) [58]. It was concluded that increase in Mn content from %12 to %15 in the high-Mn steels decreases the SFE which causes more twinning activity [34].

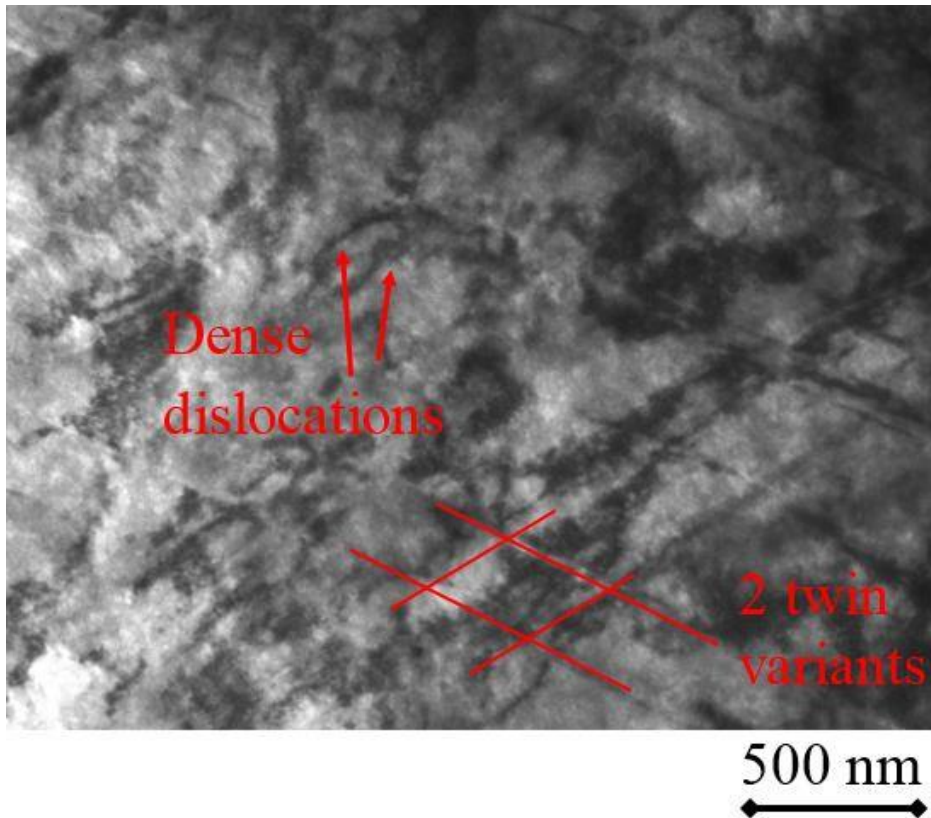


Figure 2.3. 6 TEM image of two twin variants in TWIP steel deformed at 200 °C [65].

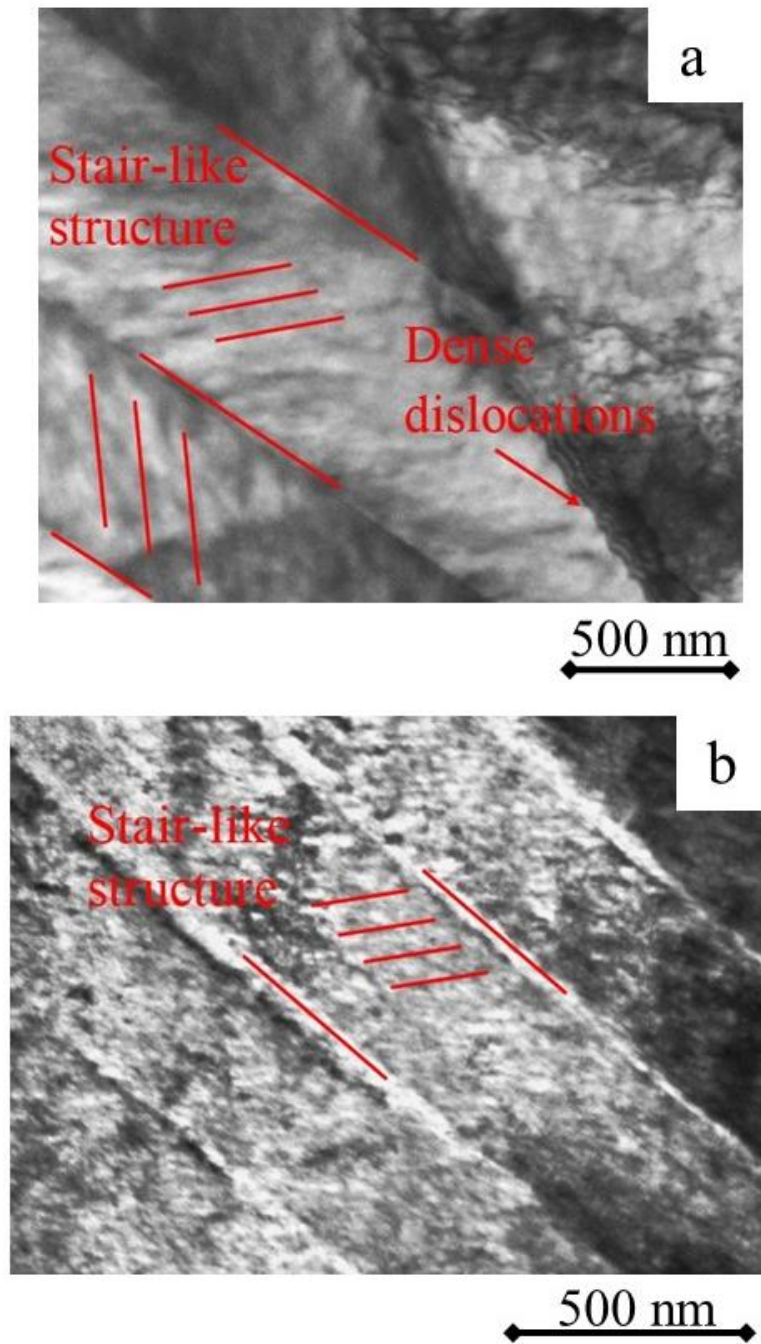


Figure 2.3. 7 TEM microstructures of TWIP steel deformed at **(a)** RT and **(b)** -170 °C [65].

However, when the Mn content reached about %20 the dominating deformation mechanism changed to be slip (Figure 2.3. 8). Also, different twin variants were activated at lower temperatures as a secondary deformation mechanism (Figure 2.3. 9(a) – 2.3. 9(b)). These results correspond well with the previous studies which were conducted on XIP steels

with similar Mn contents [61-63]. Strain rate increase causes the activation of more twin variants as well as the slip twin interactions in the microstructure of high-Mn steels [61,62]. Nevertheless, in the relatively higher strain rate study of Steinmetz et al. [63] which was conducted at several temperatures ranging from RT to 600 °C, the activation of third twin variant was not observed. Therefore, we conclude that the activation of third twin variant is observed at very high strain rates.

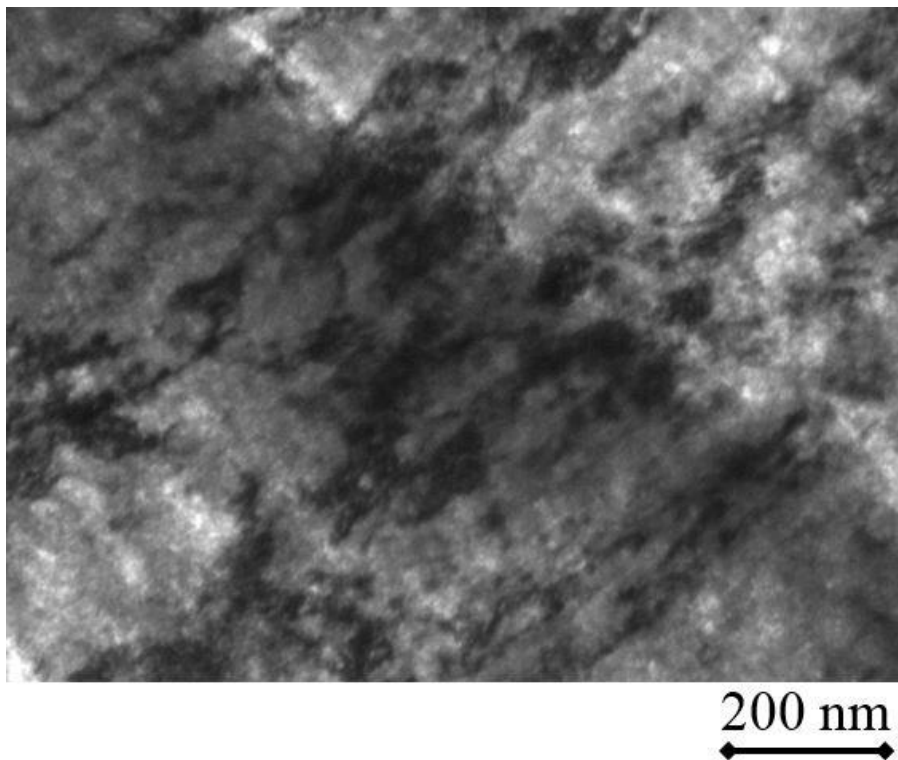


Figure 2.3. 8 TEM microstructure of XIP sample deformed at 200 °C [65].

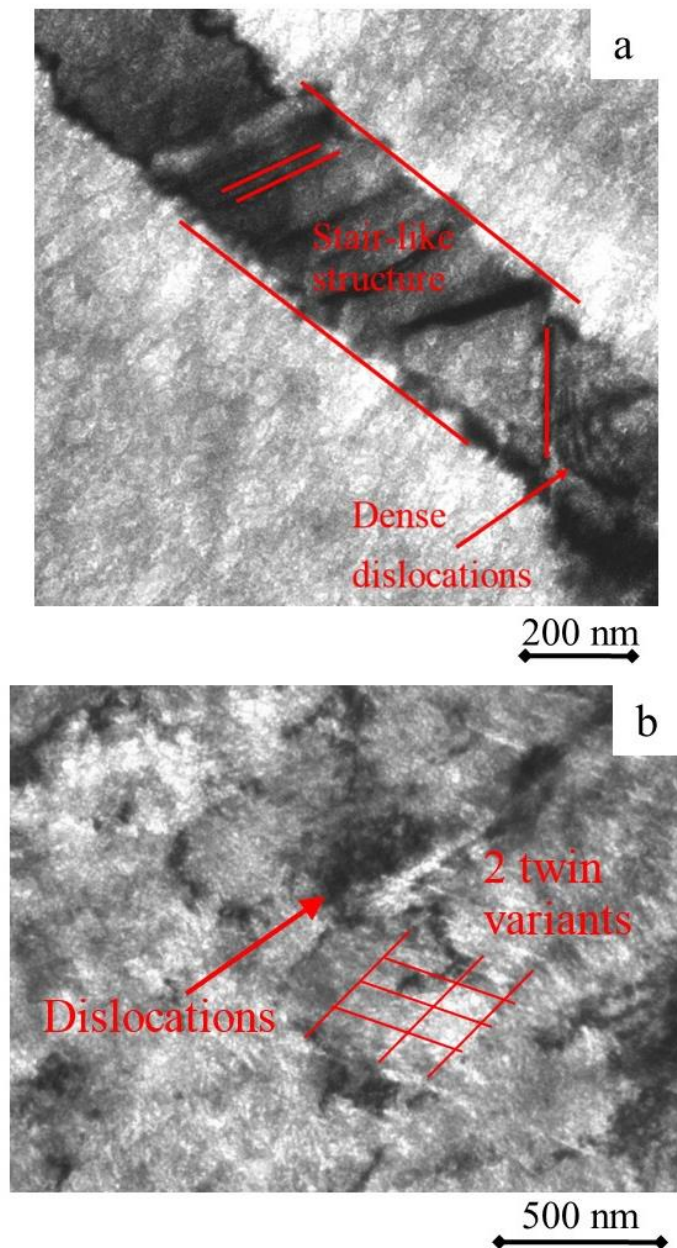


Figure 2.3. 9 TEM microstructures of XIP steel deformed at **(a)** RT and **(b)** -170 °C [65].

It is clear that the deformation behavior of Hadfield steel is dictated by various micro-deformation mechanisms at different temperatures (Figures 2.3. 2 – 2.3. 5). However, in TWIP steel deformation mechanisms are less complicated, such that, voids and slip-inside-twins were not observed. This phenomenon is related to SFE which was decreased by additional Si content in the material when compared to Hadfield steel. When SFE decreases

twinning become the dominant deformation mechanism and slip is suppressed. In addition, when the TWIP steel was deformed at lower temperatures (RT), the complexity of twin structured increased since the diffusion of atoms diminishes and slip is suppressed at low temperatures (Figure 2.3. 7(a)). As a matter of fact, further decrease in temperature (-170 °C) eradicates even the dense dislocations (Figure 2.3. 7(b)).

Since the XIP steel has the highest Mn content compared to other two samples, it has the highest SFE. In addition, the SFE is also linearly proportional to temperature. Therefore, deformation in XIP steel at high temperature was dictated by dislocation glide (Figure 2.3. 8). On the other hand, when the temperature decreased to RT and -170 °C twins, slip-twin interactions and two different twin variants were the main deformation mechanisms respectively (Figures 2.3. 9(a)- 2.3. 9(b)). Overall, loading velocity, chemical composition and temperature dependencies of deformation mechanisms were observed among three different high-Mn austenitic steels. It was observed that, nano-twins were formed during high strain rate plastic deformation at low temperatures. These nano-twin formation is also depends on the Mn content. Specifically, in Hadfield steel it was formed at all temperatures, in TWIP steel it was formed only at low temperature and in XIP steel it was formed only at RT. Consequently, the current study shed light onto the activation of different deformation mechanisms depending on the loading conditions in high-Mn austenitic steels. .

2.3.3 Conclusions

In this study, very high strain rates were applied by man-made experimental setup in order to induce enhanced twinning activity. Three different types of high-Mn austenitic steels were used as a sample. According to results which were obtained from high strain rate and low temperature tests, formation of nano-twins contributes to strain hardening of these high-Mn steels. In addition, nano-twin formation was also depends on the alloy content and

temperature. Thus, work hardening capacity of these high-Mn steels could be improved by optimizing the parameters which affect the twinning activity.

2.4 Twinning Activity in High-Manganese Austenitic Steels Under High-Velocity Loading

2.4.1 Experimental Details

In this study, two different types of high-Mn steels, namely, TWIP (15 wt. % Mn, 0.6 wt. % C, and 2.6 wt. % Si) and XIP (21 wt. % Mn and 0.6 wt. % C) steels were subjected to high-velocity tension utilizing a SHB setup, where small scale samples with a thickness of 1.6 mm were tested (Figure 2.4. 1) at temperatures ranging from -170 °C to 200 °C. A transmission electron microscope (TEM) operated at nominal acceleration voltage of 200 kV was utilized to monitor both pre- and post-experimental microstructures of the samples.

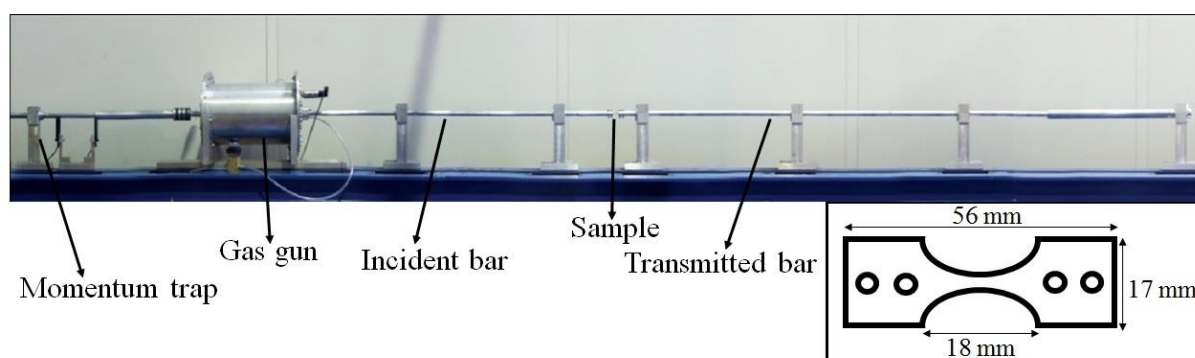


Figure 2.4. 1 The SHB setup utilized in the current work. The inset shows the sample dimensions [69].

2.4.2 Results and Discussion

The dominating micro-deformation mechanisms for both steels at each test temperature are summarized in Figure 2.4. 2, where the high Mn content (along with the Si content) decreased the SFE, leading to the TWIP effect. Although the plastic deformation of the TWIP steel was dictated by mechanical twinning at all temperatures, two different twin variants dominated the microstructure at 200 °C (Figure 2.4. 2), while nano-twin formation within primary twins was prevalent at RT (Figures 2.4. 2 and 2.4. 3(a)) and -170 °C (Figure 2.4. 2). The RT microstructure is especially interesting, such that the ladder-like structure promoted by the formation of nano-twins within primary twins apparently also affects the macro-scale fracture surface appearance (Figure 2.4. 3(b)). This is associated with the extensive formation of ladder-like twin structures on parallel planes at the micro-scale, such that a similar surface relief is also observed on the macroscopic scale [70]. Furthermore, significant dislocation activity was also evident at RT, despite the low SFE at low temperatures and high deformation velocity imposed by the SHB. This unexpected dislocation activity is attributed to the enhanced thermal energy due to rapid lattice deformation. When the temperature decreased from RT to -170 °C, however; the relative slip activity decreased, as well (Figures 2.4. 2 and 2.4 3).

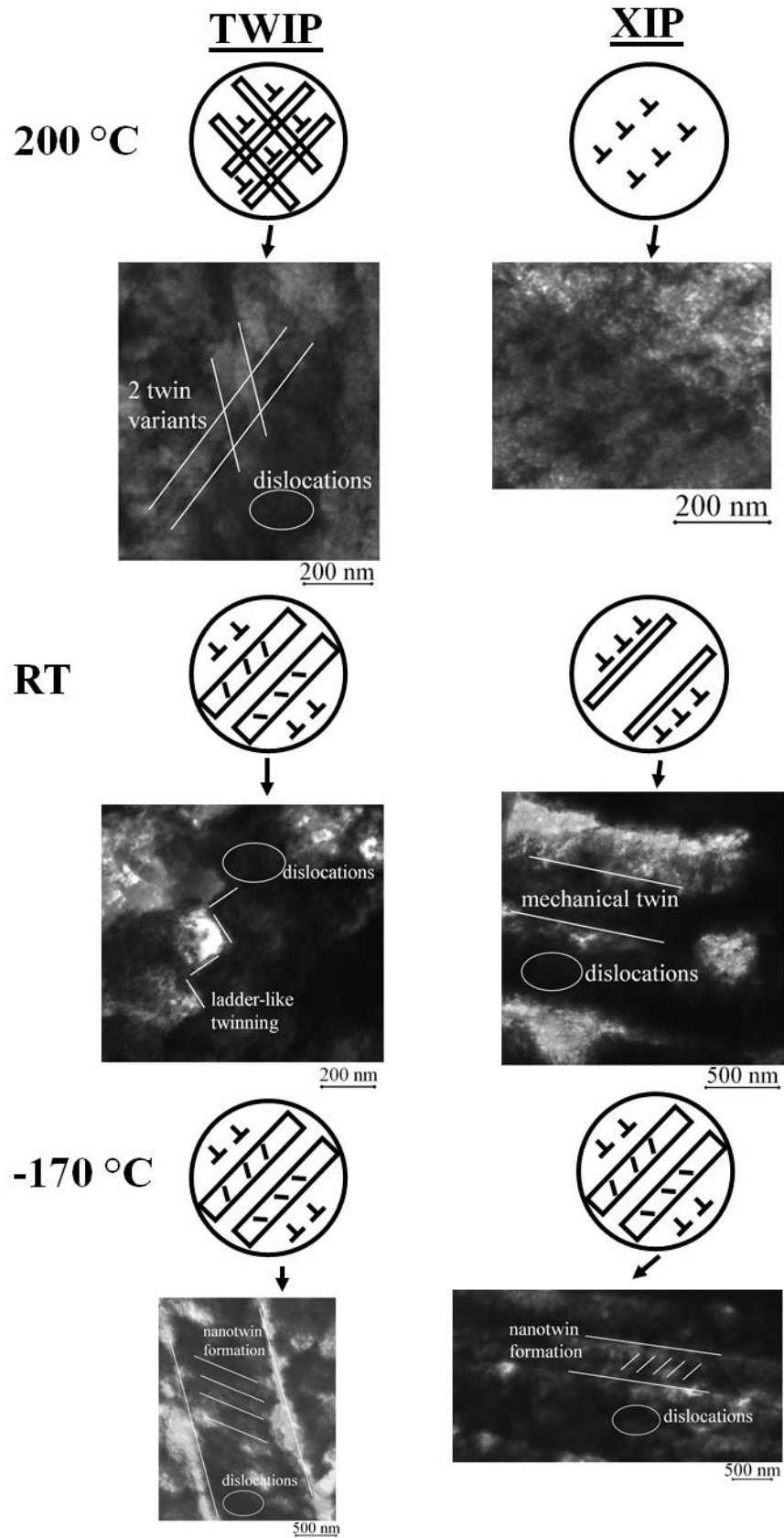


Figure 2.4. 2 Schematics and actual TEM images of TWIP and XIP steel microstructures upon loading at all three test temperatures [69].

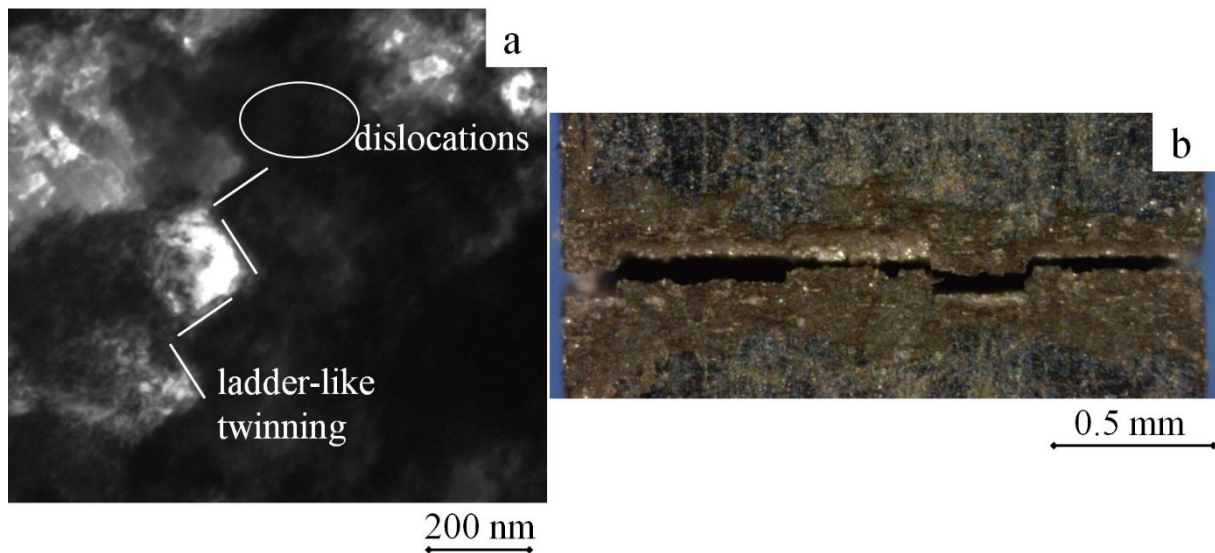


Figure 2.4. 3 TEM micrograph of TWIP steel deformed at RT showing ladder-like twin structures and dense dislocation arrangements, (b) macro-scale fractograph of TWIP steel [69].

As for the higher Mn-containing XIP steel, the deformation was dominated by slip at 200 °C due to the higher SFE attained by the higher Mn content [21]. At RT, however; only one twin variant was prevalent in addition to dense dislocation activity (Figure 2.4. 2), which differs from previous reports of two twin variants interacting with dislocation tangles for a steel with close Mn content to the current XIP steel [71]. The deformation response of XIP steel revealed lower twinning activity by increased SFE due to higher Mn content of XIP steel than in TWIP steel, which stands in good agreement with the previously reported unusual Mn-content dependence of SFE in high-Mn austenitic steels [21]. When the XIP steel was deformed at -170 °C, nano-twins formed within the primary twins (Figure 2.4. 2). This unusual twinning mode coexisted with dislocation substructures promoted by the sustained atomic displacements in the lattice during the high speed deformation (Figure 2.4. 2). Interestingly, the slip activity in XIP steel did not significantly change with temperature, as opposed to the TWIP steel, which is associated with the higher SFE of XIP steel, which makes abrupt orientation change difficult due to twin formation.

2.4.3 Conclusions

High-velocity tensile experiments carried out on a split-Hopkinson bar setup on two types of high-manganese (Mn) steels revealed the chemical composition and temperature dependencies of twinning activity in this class of steels. The results have shown the rare deformation mechanism of twinning-induced plasticity (TWIP) steel at room temperature, where ladder-like twinning was observed at both micro- and macro-levels. For the XIP steel with a higher Mn content, on the other hand, nano-twin formation within primary twins was prevalent, especially at low temperatures. The important finding is that both the ladder-like and nano-scale twin structures enhance the twin density, and hence contribute to the exceptional work hardening capacity of high-Mn steels by providing additional barriers against dislocation motion.

The analyses presented in this chapter clearly demonstrated that chemical composition plays a crucial role for the deformation response of steels. In the following chapter, a unique multi-scale modeling approach is proposed to predict the contribution of dynamic strain aging, which is mainly brought about the solute carbon atom reorientation in the core of dislocations, on the unusual strain hardening response of Hadfield steel.

2.5 References

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3 CHAPTER 3 INCORPORATION OF DYNAMIC STRAIN AGING INTO A VISCO-PLASTIC SELF-CONSISTENT MODEL

3.1 Introduction

Despite having been subject to several investigations and a topic of debate for decades, the unusual strain hardening response of Hadfield steel (HS) has not been linked to a clear cause yet. This superior steel, which exhibits high wear resistance combined with significant ductility and strength, possesses an inherent toughness and an exceptional work hardening capability [1–12]. The lattice structure is face-centered cubic (fcc) at room temperature, mainly due to chemical stabilization of austenite by carbon (C) and manganese (Mn) in the microstructure [11], resulting in improved strain hardening behavior. Previously, the unusually high strain hardening capacity of HS was often attributed to the formation of twin boundaries that provided strong barriers against dislocation motion [2,4,13–16]. In addition to twin boundaries, interruption of the glide dislocation path by stacking faults [3,17] has also been claimed as the reason for the aforementioned unusual strain hardening exhibited by HS. It was also shown that alloying of HS with aluminum (HSwAl) further increased the strain hardening rate by enhancing the formation of high-density dislocation walls (HDDWs) and their interactions with active slip systems, as demonstrated by thorough transmission electron microscopy (TEM) investigations [5,18]. A visco-plastic self-consistent (VPSC) model was proposed [5], which takes into account the interaction of HDDWs with the glide dislocations, leading to the increased strain hardening observed in single crystals of HSwAl, which then was extended to polycrystals of HSwAl [18]. The study has shown that the model is also applicable to simulate the deformation response of polycrystalline HSwAl [18].

In addition to the aforementioned arguments, dynamic strain aging (DSA) was also claimed as the reason underlying the rapid strain hardening of HS [1,12]. In particular, based on experimental observations on HS within a wide range of temperatures promoting different levels of the competing slip and twin activities, DSA, brought about by the reorientation of carbon members of Mn-C couples in the cores of dislocations, was argued to be the primary cause of rapid strain hardening in HS [1]. This argument was supported by a model that accounts for the change in the probability of possible metal-interstitial atom pairs during plastic deformation of HS, where enhanced C diffusion is facilitated by increased dislocation density [12]. Specifically, the passage of a dislocation destroys the local order, and the slip induced chemical energy change also affects the number and distribution of nearest neighbor chemical bonds, such that the distribution of metal-interstitial atom pairs also vary throughout the deformation [12]. Even though this model well demonstrated the contribution of DSA to the overall hardening [12], the results were limited to reflecting the deformation induced statistical changes in the distribution of metal-interstitial atom pairs, and the corresponding chemical energy changes.

Recently, an experimental study combining the digital image correlation with strain rate jump tests within a strain rate range of 10^{-4} to 10^{-1} s^{-1} [19] revealed that DSA indeed plays a critical role on the work hardening response of HS. Specifically, it was demonstrated that HS exhibits negative strain rate sensitivity (NSRS) within the aforementioned strain rate range, such that increasing strain rate may cause softening of the material, warranting further investigation of the contribution of DSA to the overall hardening response of HS. With this motivation, the current work focuses on the incorporation of DSA into a crystal plasticity model to predict both the role of DSA on the strain hardening behavior of HS and the previously observed NSRS exhibited by this material.

Despite the very limited number of studies focusing on DSA in HS, DSA and rate sensitivity in metallic alloys have been the subject of interest in several works, which have laid out the fundamentals and important details of DSA [20–27]. Consequently, theoretical framework of DSA was established in detail, and numerical models were proposed to predict DSA. Nevertheless, the focus of the numerical simulations was confined mostly to the statistical analysis of shear localization during deformation and the Portevin Le Chatelier (PLC) effect. Some works included numerical simulations of stress-strain response, however; neither these works nor others to follow have so far presented a thorough analysis targeting the effects of rate sensitivity on the macroscopic deformation response and its prediction.

The PLC effect brought about by the instability of dislocation motion due to solute atoms in the lattice is commonly associated with DSA, and was investigated experimentally to some extent for metallic materials. However, the atomic- and micro-scale basis of the phenomenon makes monitoring of the PLC activities difficult with conventional testing methods. Thus, many of the corresponding experimental studies employed advanced techniques, such as acoustic emission [28], digital image correlation (DIC) [29] and laser scanning extensometry [30]. However, difficulty in distinguishing the PLC effect and the signals arising from acoustic emission source, dependence of the DIC results' reliability on the sample surface preparation and imaging quality, and possibility of obtaining only one-dimensional information in laser scanning extensometry [31] make these techniques impractical. This, on the other hand, makes modeling a practical and attractive means of studying the contribution of DSA, and hence the PLC effect, to the overall work hardening behavior of metallic materials.

The current study was undertaken with the intention of clarifying the role of DSA on the strain hardening response of HS through modeling. For this purpose, a crystal plasticity model was developed incorporating DSA into standard VPSC model, where the classical

Voce type hardening was modified by taking into account the flow stress contribution that reflects the stress field imposed on the arrested dislocations due to rate dependent solute field surrounding them. The results then were compared to the experimental results obtained from strain rate jump tests on HS polycrystals. The novelty of the modeling effort presented herein lies in the implementation of the contribution of the DSA to the overall hardening response of the material, which required the proper treatment of an atomic-scale problem at the micro-scale. The simulation results demonstrated the success of the proposed model in predicting the role of DSA on the mechanical response of the HS, including the NSRS exhibited by this material. Overall, the new model proposed in this paper opens a venue for proper treatment of DSA and predicting the NSRS in rate sensitive metallic materials.

3.2 Materials and Methods

The material investigated in this study is HS with a chemical composition of 12.44 wt. % Mn, 1.10 wt. % C and balance Fe, and a face-centered cubic (fcc) structure. The samples were extracted from railroad frogs taken from service. Electro-discharge machining was utilized to cut small-scale dog-bone shaped tension specimens. The samples were tested utilizing a servo-hydraulic test frame equipped with a digital controller. A miniature extensometer with a gauge length of 3mm was employed for accurate strain measurement in the gauge section. Two types of experiments were carried out under tensile loading: Monotonic stress-strain experiments and strain rate jump tests. The experiments were conducted at strain rates within the range of 10^{-4} to 10^{-1} s^{-1} . The samples were analyzed with X-Ray Diffraction (XRD) prior to experiments in order to determine the initial textures in the loading direction.

At room temperature, HS exhibited NSRS in the strain rate range of 10^{-4} to 10^{-1} s^{-1} as shown in Figure 3. 1. Moreover, stress drops due to flow localization follow a periodic pattern, typical of PLC effect [19]. Figure 3. 2 presents the results of strain rate jump test, further demonstrating the NSRS of HS. An abrupt change in the strain rate results in an instantaneous change in flow stress, $\Delta\sigma_i$, which is always positive [25], and this change in the deformation response is reflected by the instantaneous strain rate sensitivity, denoted by $M_i = \frac{d\sigma_i}{d \ln \dot{\epsilon}}$. However, whether the strain rate sensitivity is negative or positive is based on the steady state strain rate sensitivity, $M_s = \frac{d\sigma_{ss}}{d \ln \dot{\epsilon}}$, which considers the difference in stable flow stress, $\Delta\sigma_{ss}$, following the strain rate jump [25,26]. In the negative strain rate sensitivity regime, $\Delta\sigma_{ss}$ and M_s are negative, and becomes positive outside the negative strain rate sensitivity regime (Figure 3. 2).

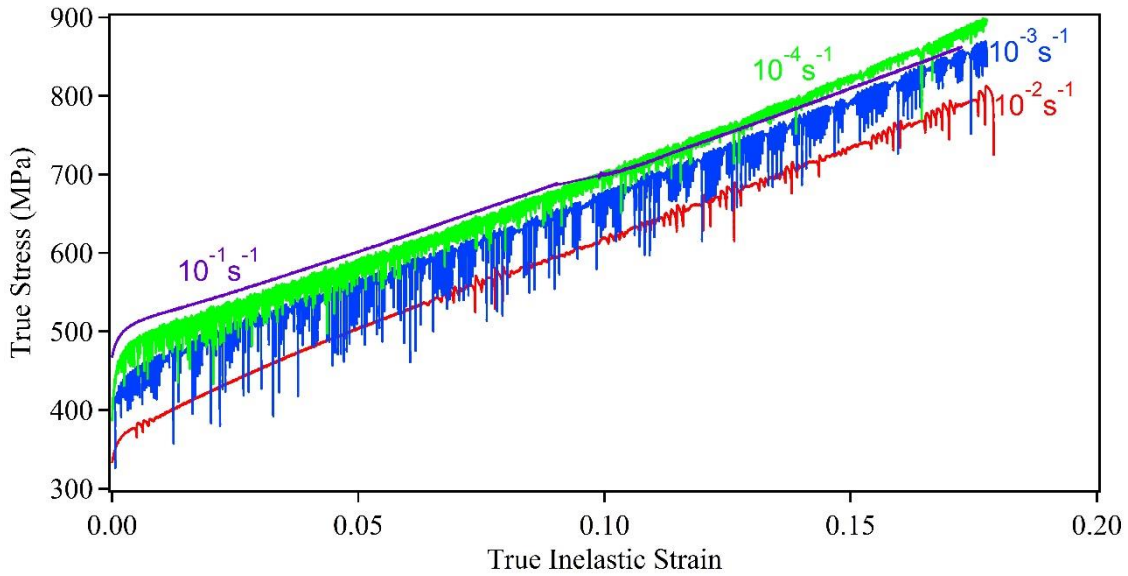


Figure 3. 1 The room temperature uniaxial tensile deformation response of HS obtained at different strain rates. The data were recompiled from [32].

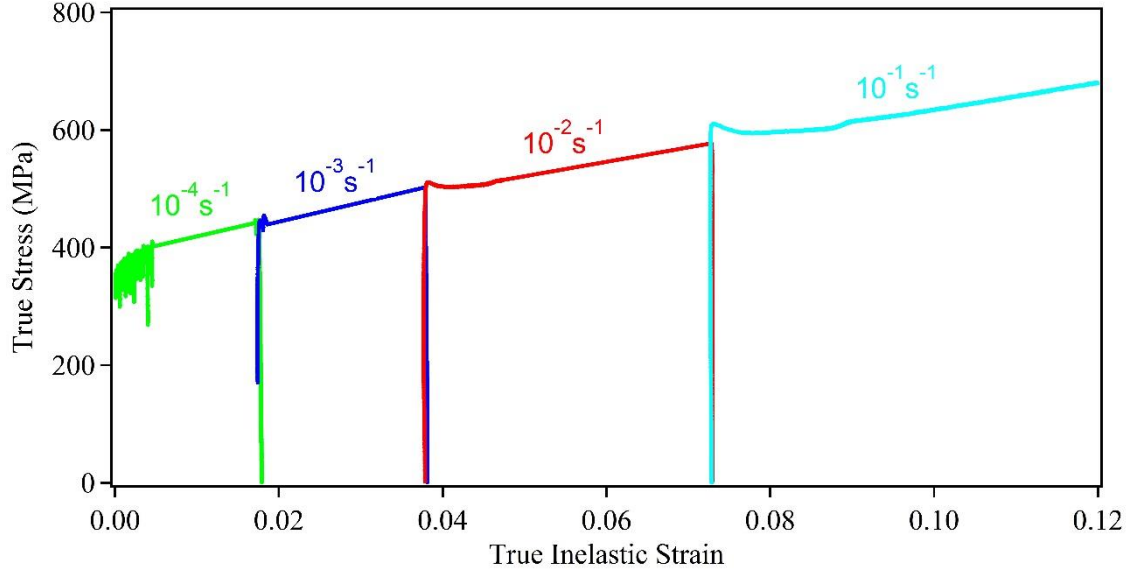


Figure 3. 2 Results of a representative strain rate jump test. The data were recompiled from [32].

3.3 Theory and Calculations

3.3.1 Modeling the Role of Dynamic Strain Aging on Strain Hardening

In order to better understand the influence of DSA on the deformation response of HS, the DSA was incorporated into standard VPSC model as an additional mechanism affecting the strain hardening. The classical Voce hardening scheme was modified to accomplish this, such that the role of DSA was expressed in terms of shear stress field imposed on arrested dislocations due to surrounding carbon atom field. The details of this unique formulation are presented in this section.

The DSA as a phenomenon is attributed to the pinning of mobile dislocations arrested at obstacles, by solute atoms diffusing in the matrix [22]. Upon the hindering of dislocation glide by obstacles, there is an elapse of time before the dislocations overcome the obstacles. The average time the dislocations stay arrested at obstacles throughout the matrix is defined as the waiting time, t_w and is proportional to the density of mobile dislocations (ρ_m), the

Burgers vector magnitude (b), the dislocation mean free path (L), and the inverse of strain rate ($1/\dot{\epsilon}$). Hence, the Orowan equation defines the waiting time as $t_w = \rho_m b L / \dot{\epsilon}$ [22,25,26]. During the waiting time, solute atoms might diffuse into the arrested dislocations, leading to DSA [22]. Overall, DSA depends on temperature, time of arrest of dislocations at the obstacles (t_w), strain rate, solute concentration, and diffusion coefficient. As the waiting time is directly related to strain rate, consequently, DSA is expected to influence the dependence of stress on the strain rate. Previously, the influence of the DSA on the flow stress was taken into account through an Arrhenius-based constitutive relationship [25,26]. In this study, we consider the contribution of DSA to the critical resolved shear stress in each grain (or single crystal). The contribution due to DSA was taken into account through the additional shear stress on the arrested dislocations due to the diffusing solute atoms pinning them [33]. The role of carbon solute field around arrested dislocations is considered under conditions where carbon is in equilibrium with local stresses [33]. All the mobile dislocations that are pinned by the diffusing solute carbon atoms are considered to be positive edge dislocations for the sake of simplicity. In the current study, the shear stress imposed on a positive edge dislocation due to carbon atom is modeled by a continuous distribution of dilatation lines whose strength depends on the local carbon concentration around arrested edge dislocations.

With respect to solute concentration, the velocity of solute atoms relative to a positive-edge dislocations that move in the direction of the unit vector $\underline{i}$ is considered to consist of three components [21]: The drift velocity $\underline{v}_1 = \frac{-D\underline{\nabla}W^{\text{int}}}{kT}$ due to the field of force $-\underline{\nabla}W^{\text{int}}$, diffusion velocity $\underline{v}_2 = -\frac{D\underline{\nabla}C}{C}$ due to concentration gradients, and a constant velocity $\underline{v}_i$ due to dislocation motion. The field of force $-\underline{\nabla}W^{\text{int}}$ is simply the negative gradient of the interaction energy, W^{int} , and C , D , k and T represent the solute atom distribution,

diffusion coefficient, Boltzmann's constant and the absolute temperature, which was taken as 298 K in the current work, respectively. As a result, the velocity of solute atoms relative to dislocations is given by [21]:

$$\underline{v} = \underline{v}_1 + \underline{v}_2 + \underline{v}_i = -\frac{D\underline{\nabla}W^{\text{int}}}{kT} - \frac{D\underline{\nabla}C}{C} + \underline{v}_i \quad (1)$$

The interaction energy (W^{int}) between a positive edge dislocation and an atom in substitutional solution is defined as [20]:

$$W^{\text{int}}(r, \alpha) = \frac{4}{3} \mu \chi r_a^3 b \frac{1 + \nu}{1 - \nu} \frac{\sin \alpha}{r} \quad (2)$$

The terms r and α define the cylindrical coordinate system with the positive edge dislocation at the origin (Figure 3. 3). The atomic radii of the solvent and solute atoms are given by r_a and $r_a(1 + \chi) = r_c$, respectively. Poisson ratio and modulus of rigidity are represented by ν and μ , respectively.

Assuming steady state of motion, the continuity condition requires that $\underline{\nabla}(C\underline{v}) = 0$, which eventually yields the solute atom concentration function as [21]:

$$C(r, \alpha) = C_0 \exp \left\{ -\frac{W^{\text{int}}(r, \alpha)}{kT} \right\} \quad (3)$$

where C_0 is the average solute concentration of the alloy.

In this basic form of Eq. 3, however; the solute atom concentration distribution remains valid for steady state equilibrium, and does not reflect the time dependency, which is crucial for DSA. This time dependency of the solute atom concentration was well established in previous work [25,26]. Accordingly, the solute atom concentration is expressed as:

$$C(r, \alpha) = C_0 \exp \left\{ \left(K(r, \alpha) D t_a \right)^{2/3} \right\} \quad (4)$$

In Eq. 4, the term $K(r, \alpha)D$ is the inverse of characteristic solute diffusion time, t_d , such that $t_d = (K(r, \alpha)D)^{-1}$ [26]. Thereby, both the time dependency of the solute atom concentration and the competing velocities of diffusion and dislocation motion are taken into account in the definition of the solute atom concentration, $C(r, \alpha)$. The term $K(r, \alpha)$ includes the solute-dislocation binding energy, and t_a represents the aging time, which is the effective time period for which the dislocations are aged. It was shown that the effective aging time of the dislocations (t_a) by the solute atoms pinning them is less than the waiting time, t_w , and therefore is used to establish the time dependency of the solute atom concentration [25]. The aging time is related to the waiting time as [25,34,35]:

$$\frac{dt_a}{dt} = 1 - \frac{t_a}{t_w} \quad (5)$$

Considering the definition of the waiting time given by the Orowan equation, the aging time t_a is a function of strain and strain rate history. Thus, the time dependency of t_a determines the transient behavior of the solute concentration, $C(r, \alpha)$. From Eq. 5, it also follows that the aging time will be equal to the waiting time, i.e. $t_a = t_w$, only for steady state conditions [25]. For non-steady state case, the time dependent average waiting time is a function of fundamental attempt frequency, ν_o , and energy barrier, E , which depends on the effective resolved shear stress, τ_{eff} , acting on current time t [36–38]. The attempt frequency depends on mobile dislocation density, burgers vector and the Debye frequency, ν_D , which is a function of both density of the lattice and the speed of sound [39]. Specifically, the average waiting time can be expressed as:

$$t_w = e^{\Delta E(\tau_{eff}^\alpha)/kT} / \nu_o \quad (6)$$

Several energy barrier models were proposed associated with different kind of obstacles [26,40–42]. For short-range obstacles, which are more sensitive to thermal activation, Kocks suggested a useful phenomenological generalization of stress-dependent energy barrier model as (Kocks et al., 1975):

$$E(\tau_{eff}^\alpha) = E_0 \left[1 - \left(\frac{\tau_{eff}^\alpha}{s_{t0}} \right)^p \right]^q \quad (7)$$

where E_0 is zero effective shear stress activation energy, p and q are the profiling parameters and constant s_{t0} is thermal slip resistance at 0 K, i.e. Peierls stress [39]. Initial effective shear stress activation energy and Peierls stress values were taken for an host iron matrix [39], assuming that an iron matrix represents the Hadfield steel matrix, since it is extremely difficult to model the actual Hadfield steel matrix owing to the large number of constituent elements [33]. Taking profiling parameters p and q , 1/2 and 3/2, respectively, is adequately accurate for all systems [43].

In order to model the energy barrier, the effective shear stress needs to be calculated. The effective resolved shear stress on slip system α can be formulated as the difference between resolved external stress, τ , and summation of resolved back stress representing the slip system resistance, s_α , and constant thermal stress, τ_α [38,39,44,45].

$$\tau_{eff}^\alpha = |\tau^\alpha| - s_\alpha^\alpha - \tau_\alpha^\alpha \quad (8)$$

Constitutive law for elastic materials includes the second Piola-Kirchhoff stress tensor T^* , and the right Cauchy-Green strain tensor, $C^* = F^{*T}F^*$ whereas in isotropic elastic materials Cauchy stress tensor is a function of the left Cauchy-Green strain tensor, $B^* = F^*F^{*T}$. Since elastic stretch can be neglected in metallic materials, τ^α can be expressed as [39,46–48]:

$$\tau^\alpha = (C^*T^*):s_0^\alpha \cong T^*:s_0^\alpha \quad (9)$$

The resolved back stress comes into picture because of both short-term and long-term dislocation interactions during dislocation motion on the slip systems and it can be expressed using Taylor hardening model as [39,45,49]:

$$s_a^\alpha = \mu b \sqrt{\sum_{\alpha=1}^N q_p A^\alpha \rho_{total}^\alpha} \quad (10)$$

where q_p is dislocation barrier strength, A^α is the slip system dislocation interaction coefficients matrix and ρ_{total}^α is the slip system dislocation density which is the summation of mobile and immobile dislocations.

Accordingly, the shear stress, τ_{CD} , imposed on a positive edge dislocation due to the surrounding solute atom concentration is given by [33,50]:

$$\tau_{CD} = -\frac{\mu}{2\pi(1-\nu)} \frac{V_C}{N_A} \int_0^{2\pi} \int_{r_i}^{r_o} C(r, \alpha) \frac{\sin 2\alpha}{r} dr d\alpha \quad (11)$$

In Eq. 11, the terms V_C and N_A represent the partial molar volume of carbon and the Avogadro's number (6.024×10^{23} molecules/mole). The inner and outer cut-off radii of the carbon atmosphere surrounding the edge dislocation are given by r_i and r_o , respectively. It should be noted that the interaction energy given by Eq. 2 is not valid at $r_i = 0$ because the elastic continuum theory is not applicable at the origin (Figure 3. 3). Based on previous work, $r_i = b$ and $r_o = 10 \cdot b$ are assigned as the integration limits for Eq. 11.

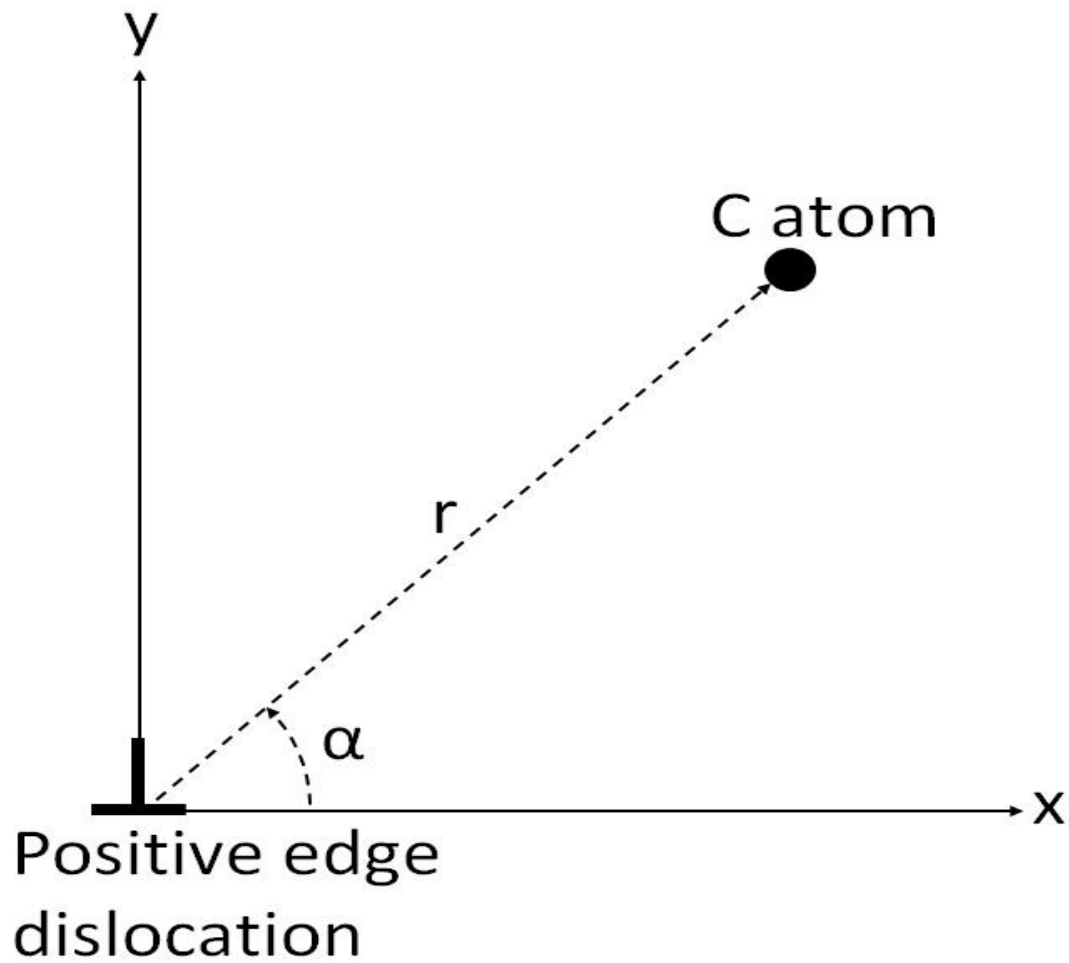


Figure 3. 3 Cylindrical coordinate system utilized to describe the location of an interstitial C atom with respect to a positive edge dislocation [32].

The shear stress given by Eq. 11 represents the additional shear stress on a single edge dislocation due to the surrounding solute (carbon) atom concentration. To be able to account for the solute effect on the flow stress, we consider the quantity given by Eq. 11 to represent an average value throughout each grain, implying that the hardening formulation needs to be modified to include this average contribution in order to account for DSA influence on the overall hardening response. The constants utilized in the current DSA model are presented in Table 3. 1.

Table 3. 1 The parameters and constants utilized in the current DSA model [32].

k	b	ν	μ	r_a
$6.61 \times 10^{-5} \text{ eV K}^{-1}$	$2.58 \times 10^{-10} \text{ m}$	0.3	71 GPa	$126 \times 10^{-12} \text{ m}$
V_C	r_c	ν_D	E_0	s_{t0}
$1.24 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$70 \times 10^{-12} \text{ m}$	$1.38 \times 10^{13} \text{ s}^{-1}$	0.57 eV	1.04 GPa

3.3.2 Modeling of Slip-Dominant Deformation Behavior in the Presence of DSA

The modified VPSC algorithm utilized in this study accounts for the deformation in the plastic zone only, and considers the plastic deformation to take place when one or more slip or twinning systems become active. The classical Voce hardening scheme [51] is utilized to define the work hardening of the material, such that the microscopic flow stress is updated for each increment according to the following equation:

$$\dot{\tau} = \sum_n \left\{ \theta_0 \left(\frac{\tau_s - \tau}{\tau_s - \tau_0} \right) \right\} |\dot{\gamma}^n| \quad (12)$$

where θ_0 is the constant strain hardening rate and τ_0 is the reference strength, which is usually taken as the initial microscopic yield strength calculated based on the experimental macroscopic yield strength[5]. The term τ_s represents the saturation stress in the absence of geometric effects, or the threshold stress, while the shear strain rate of the n^{th} active system is represented by $\dot{\gamma}^n$. The hardening can be defined by an extended Voce law [5], which is characterized by the evolution of the threshold stress (τ^s) with accumulated shear strain (Γ) in each grain:

$$\tau^s = \tau_0 + (\tau_1 + \theta_1 \Gamma) \left(1 - \exp \left(-\frac{\theta_0 \Gamma}{\tau_1} \right) \right) \quad (13)$$

where τ_0 is the reference strength, and τ_1 , θ_0 and θ_1 are the parameters that define the hardening behavior. The hardening law defined by Eq. 13 characterizes the onset of plasticity and the saturation of threshold stress at larger strains. When modified to account for the contribution of DSA, the classical Voce hardening scheme becomes:

$$\dot{\tau} = \sum_n \left\{ \theta_0 \left(\frac{\tau_s - \tau}{\tau_s - \tau_0} \right) \right\} |\dot{\gamma}|^n + M_i S \frac{d\tau_{CD}}{dt} \quad (14)$$

where M_i is the instantaneous strain rate sensitivity that takes into account the abrupt strain rate changes during deformation, and S is the scaling factor that reflects the contribution to hardening throughout the whole grain. The term $\frac{d\tau_{CD}}{dt}$ denotes the time derivative of τ_{CD} , i.e. Eq. 11, and by substitution of Eq.s 4 and 5 into the time derivative of Eq. 11, one obtains:

$$\frac{d\tau_{CD}}{dt} = -\frac{\mu}{2\pi(1-\nu)} \frac{V_C}{N_A} \int_0^{2\pi r_0} \int_{r_i} \frac{2C_0 [K(r, \alpha) D]^{2/3} \exp[(K(r, \alpha) D t_a)^{2/3}]}{3t_a^{1/3}} \left(1 - \frac{t_a}{t_w} \right) \frac{\sin 2\alpha}{r} dr d\alpha \quad (15)$$

Consequently, in its extended form, the modified Voce hardening rule can be obtained from Eq.s 13, 14 and 15 as in the following expression:

$$\begin{aligned} \tau^s = & \tau_0 + (\tau_1 + \theta_1 \Gamma) \left(1 - \exp\left(-\frac{\theta_0 \Gamma}{\tau_1}\right) \right) \\ & - S \frac{\mu}{2\pi(1-\nu)} \frac{V_C}{N_A} \int_0^{2\pi r_0} \int_{r_i} \frac{2C_0 [K(r, \alpha) D]^{2/3} \exp[(K(r, \alpha) D t_a)^{2/3}]}{3t_a^{1/3}} \left(1 - \frac{t_a}{t_w} \right) \frac{\sin 2\alpha}{r} dr d\alpha \end{aligned} \quad (16)$$

3.4 Results and Discussion

The new hardening model detailed in Section 3 was incorporated into VPSC along with the experimentally measured initial textures of HS polycrystalline samples in order to

predict the macroscopic deformation response of this material under uniaxial tensile loading with (Figures 3. 4-3. 7) and without (Figures 3. 8-3. 11) accounting for the presence of DSA and NSRS. The true stress - true inelastic strain data were plotted in order to compare the initial and modified VPSC simulations and experimental response. One should also note that only the plastic deformation regime was modeled in the VPSC simulations since the VPSC only considers active plastic deformation up to necking, which is acceptable considering that the elastic deformation response of HS is not rate dependent [19].

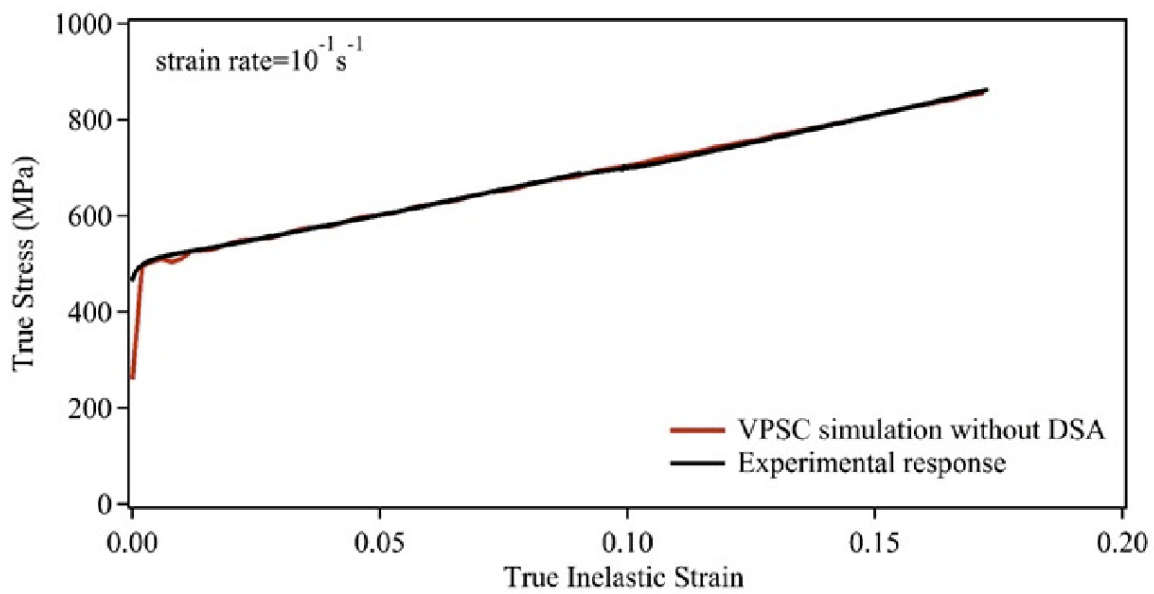


Figure 3.4 Comparison of experimental and VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-1} \text{ s}^{-1}$ [32].

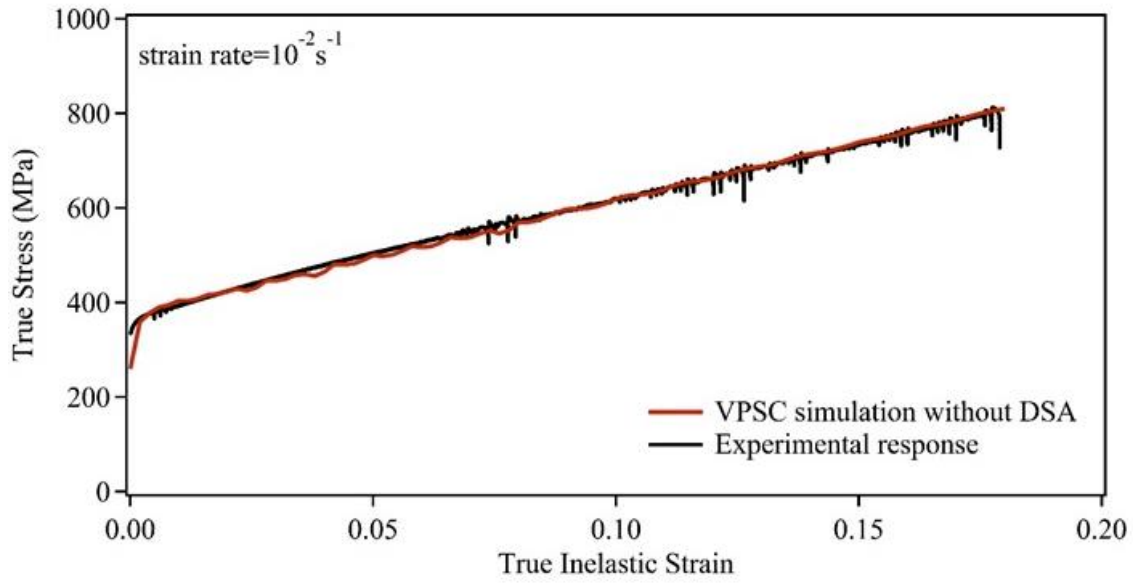


Figure 3.5 Comparison of experimental and VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ [32].

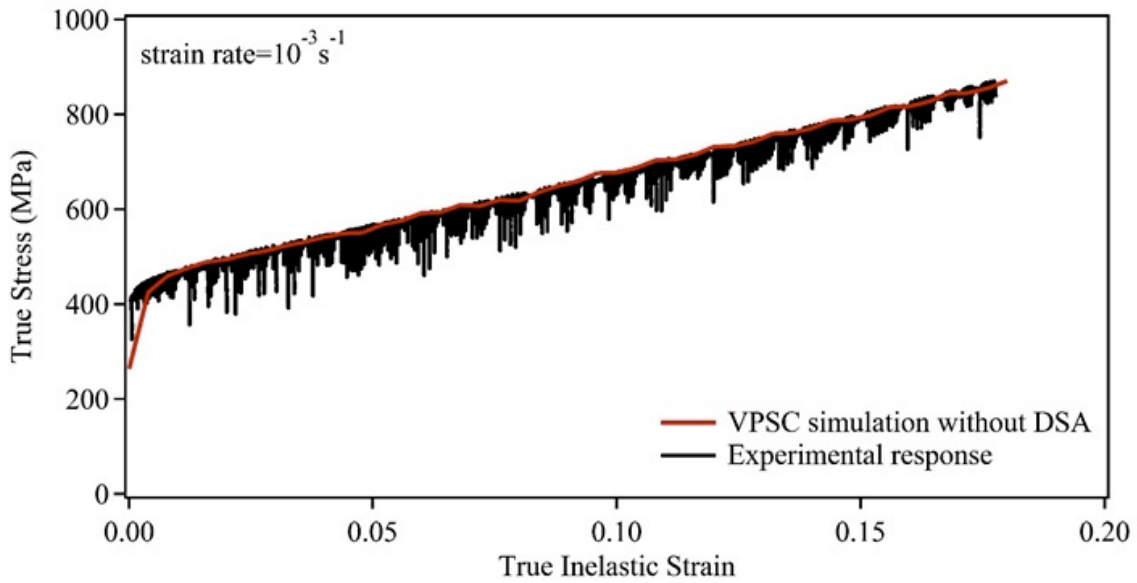


Figure 3.6 Comparison of experimental and VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ [32].

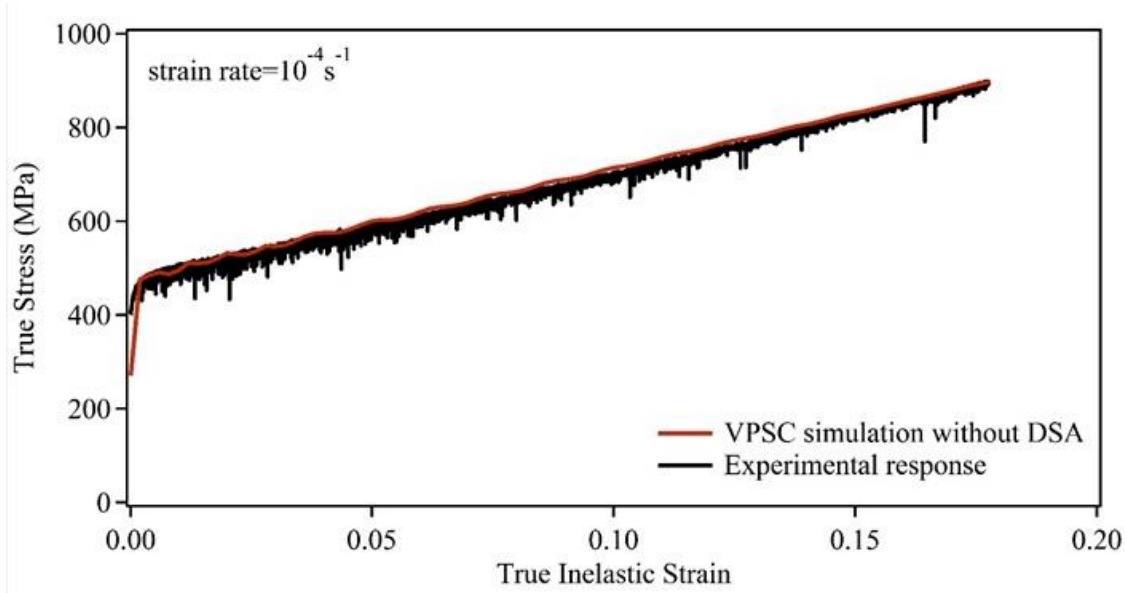


Figure 3.7 Comparison of experimental and VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ [32].

It has been recently proven that the correct prediction of the macroscopic deformation response under any type of loading scenario can be achieved by the proper modeling of the micro-scale deformation based on the experimental data obtained from even the simplest case of the uniaxial tensile deformation [52,53]. Furthermore, the VPSC model has the strength of allowing for modifications of the hardening rule, which enables to account for the microstructural features and micro-deformation mechanisms specific to each material. In particular, the deformation response of HS was previously modeled with VPSC to successfully account for the roles of several parameters on the strain hardening of this material, including slip-twin interactions, high-density dislocation walls and precipitates [4,5,54]. Based on this previous experience, the DSA model proposed herein was incorporated into VPSC, which - to the best of the authors' knowledge - constitutes the first example of incorporation of an atomic-level DSA model into crystal plasticity to predict the contributions of DSA and the resulting NSRS on the work hardening response of HS. The novelty of the current approach is the computation of the shear stress contribution imposed on

arrested dislocations leading to DSA at the atomic level, which is then implemented to the overall strain hardening rule at the microscopic level utilizing VPSC.

For this purpose, the microscopic deformation response of HS was modeled at each strain rate using the experimental uniaxial deformation response at room temperature (Figures 3. 4-3. 7). The standard VPSC model [55] was employed to predict the microscopic deformation response at each strain increment. The reference strength of slip was calculated as 132 MPa (Table 3. 2) based on Taylor's analysis [56,57], and is provided in Table 3. 2 along with the other Voce hardening parameters that were obtained by fitting the simulated deformation response to the experimental one for each strain rate (Figures 3. 4-3. 7). In particular, these hardening parameters were determined by a step-by-step procedure based on a secant type of inclusion-matrix interaction, utilizing the experimentally determined initial texture, crystal structure and number of grains of the material as input, and the experimental deformation response as a means of validation (Figure 3. 4-3. 7). Material response accounting for DSA was modeled until moderate strain values, and the shape change of the grains were not considered during the simulations.

Table 3. 2 Voce hardening parameters utilized in VPSC simulations for each strain rate [32].

Strain rate (s^{-1})	τ_0 (MPa)	τ_1 (MPa)	θ_0 (MPa)	θ_1 (MPa)
1×10^{-1}	132	925	53×10^4	350
1×10^{-2}	132	147	43×10^3	408
1×10^{-3}	132	1580	60×10^4	390
1×10^{-4}	132	918	55×10^4	398

It should be noted that the second term of the Eq. 14, which represents the contribution of DSA to the strain hardening capacity was ignored in the first set of standard VPSC simulations (Figures 3. 4-3. 7). Accordingly, the results presented in Figures 3. 4-3. 7 clearly

demonstrate that the general work hardening trend can be captured for all four strain rates, however, the repeating stress striation patterns stemming from local instabilities in the stress-strain state facilitated by DSA and specific to each strain rate cannot be predicted.

The modified VPSC simulations, where the contribution of DSA was taken into account through the new hardening rule presented in Eq. 16, considered only primary slip with 12 systems. The same Voce hardening parameters were utilized as in the case of standard simulations in order to follow the same hardening trend and observe the contribution of the new atomic-scale model. The scaling factor S of the Eq. 14 was determined as 0.93 while predicting the experimental deformation response during modified VPSC simulations. The corresponding modified VPSC simulation results are presented in the Figures 3. 8-3. 11 for the strain rates of 10^{-4} to 10^{-1} s^{-1} : The predicted deformation curves not only follow the correct hardening trend for each strain rate, but also reflect the effect of DSA on the strain hardening, which is evident from the close prediction of the repeating stress striation patterns specific to each strain rate utilizing the same model.

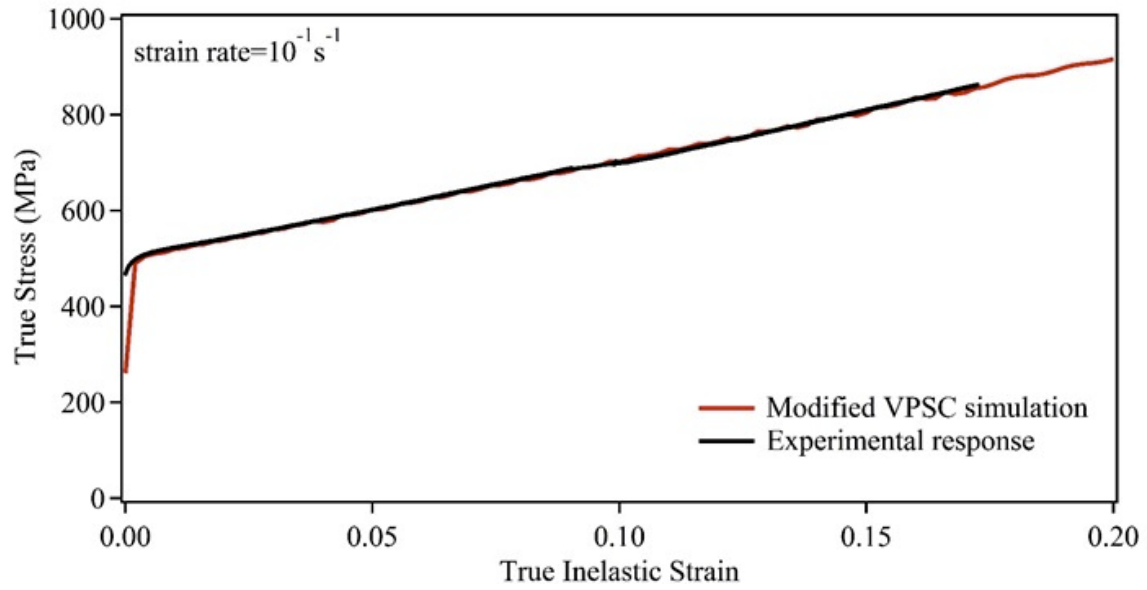


Figure 3.8 Comparison of experimental and modified VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-1} \text{ s}^{-1}$ [32].

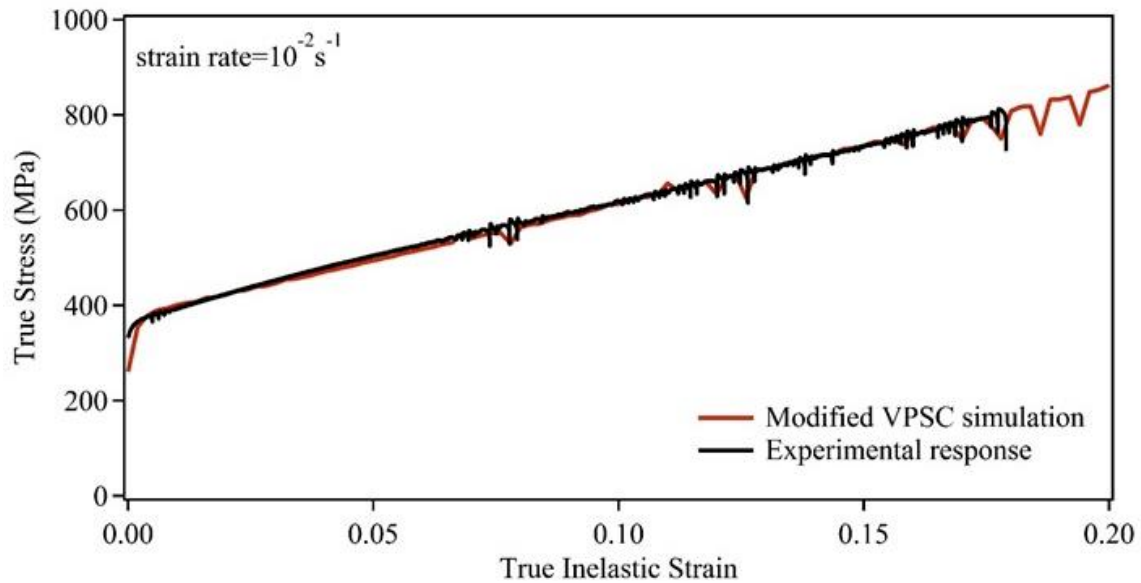


Figure 3.9 Comparison of experimental and modified VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ [32].

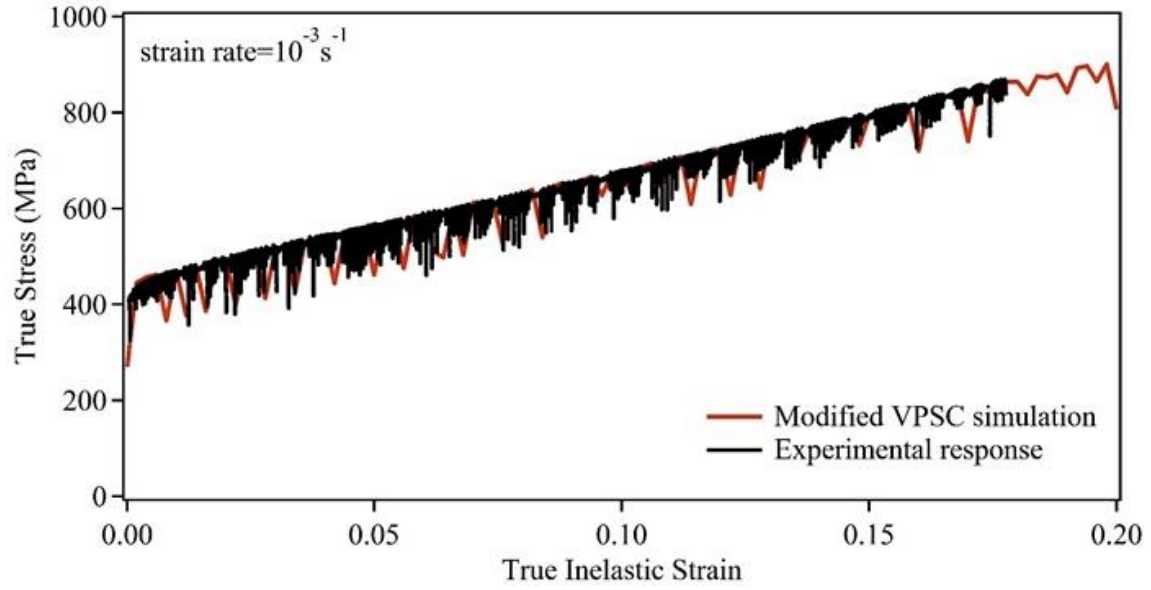


Figure 3.10 Comparison of experimental and modified VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ [32].

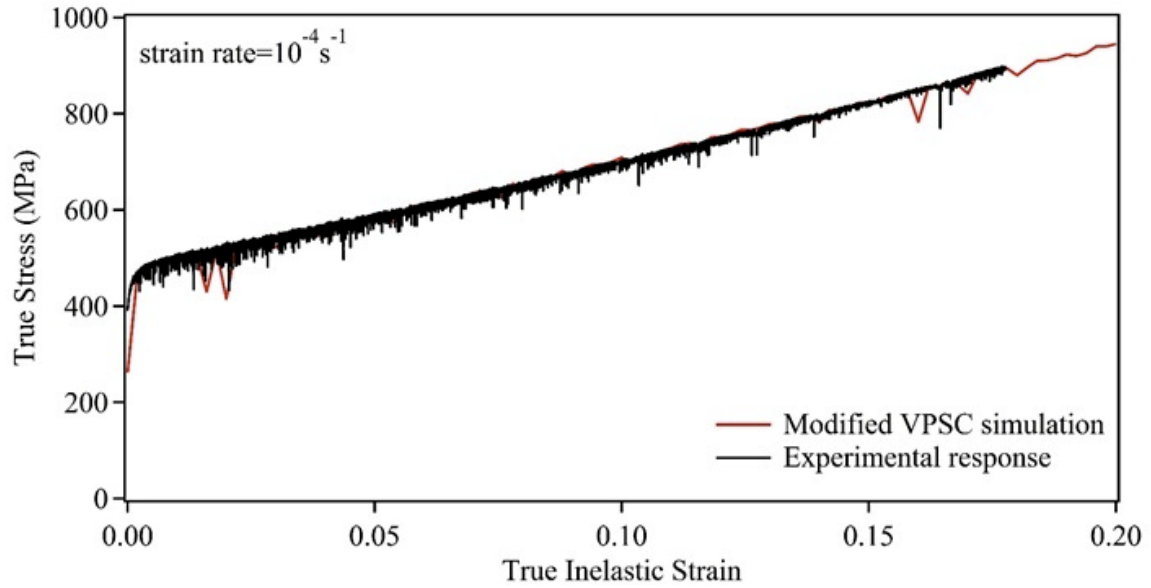


Figure 3.11 Comparison of experimental and modified VPSC simulation results of the the uniaxial tensile deformation response of HS at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ [32].

It is important to note that an increase in the strain rate causes a decline in the waiting time as the Orowan equation suggests, which implies that the C atoms pin the dislocations for a lesser time period. However, increase in strain rate provides additional energy to the system, which should be dissipated by the dislocation movements, C atom diffusivity or other

microstructural interactions. Analytically, the waiting time has significant effect on the time derivative of τ_{CD} , as the Eq. 15 suggests. Nevertheless, this term also depends on aging time, which is also a function of the waiting time. Therefore, based on the analytical and conceptual descriptions, it cannot be concluded that C effects on the deformation response of HS varies at each strain increment, which causes plastic instabilities during the material flow that are more pronounced at low strain rates [14,19]. The current model successfully predicts such plastic instabilities both at the low and moderate inelastic strain values (Figures 3. 8-3. 11), such that the instantaneous changes in the material response can be well represented. Overall, the new crystal plasticity modeling approach not only predicts the relatively more stable deformation response at high strain rates (e.g., 10^{-1} s^{-1} , Figure 3. 8), but also provides a very good estimate of the unstable plastic deformation response exhibiting larger stress striations at lower strain rates (Figures 3. 10 and 3. 11). Moreover, the current model successfully captures the NSRS exhibited by HS, which ensures that the current approach can be adopted to predict the deformation response of rate-sensitive metallic materials.

3.5 Conclusions

A new crystal plasticity modeling approach was proposed to predict the roles of dynamic strain aging (DSA) and the resulting negative strain rate sensitivity (NSRS) on the unusually high work hardening capacity of Hadfield steel (HS). For this purpose, the room temperature macroscopic deformation response of HS polycrystals was examined with the aid of monotonic and strain jump experiments under uniaxial tensile loading within the 10^{-4} to 10^{-1} s^{-1} strain rate range. Specifically, a unique strain hardening model was proposed that incorporates the atomic level local instabilities due to the pinning of dislocations by diffusing carbon atoms to the classical Voce hardening. The simulation results demonstrated that the

new modeling approach presented herein not only successfully predicts the role of DSA and the resulting NSRS on the macroscopic deformation response of HS, but also opens a new venue for accurately predicting the deformation response of rate-sensitive metallic materials.

The knowledge gained in this study was further extended to deepen the understanding of the mechanics of hydrogen embrittlement in metallic hydrogen storage materials through an experimentation and a multi-scale modeling approach.

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4 CHAPTER 4 TACKLING A CRITICAL PROBLEM IN HYDROGEN STORAGE: CRACK PROPOGATION IN THE PRESENCE OF HYDROGEN

4.1 Introduction

Hydrogen (H) interstitials can promptly diffuse into metallic materials and alloys and expand the crystal lattice isotropically. Thus, diffused H alters the mechanical properties of the host material at micro-, meso- and macro-scales [1,2]. H embrittlement (HE) which is a degradation mechanism that leads to catastrophic failure for metallic materials exposed to H, is a very important factor affecting the safety, design procedure and maintenance of various applications, such as H storage, thermo-nuclear reactors, next generation automobiles, gas- and oil- pipelines, and renewable energy and fuel cells [3–6]. Since the microstructures of H-induced materials are more complicated than those of the H-free materials in terms of micro-deformation mechanism activities and interactions due to the presence of H, HE turns out to be one of the most exhaustive degradation and failure mechanisms in metallic materials [7].

The scientific investigation of HE began with the pioneering report of W. H. Johnson in 1875, where HE was defined as the temporary decrease of the materials' toughness and fracture stress upon H diffusion, which is followed by recovery of the original mechanical properties [8]. Numerous researchers focused on HE to date, and the corresponding presence of dissolved H has been demonstrated to reduce ductility, which changes the fracture mode from ductile transgranular to brittle intergranular, enhances the crack growth rate, and reduces the fracture strength and energy absorption capacity of a material at the macroscopic scale [9–11]. This, in turn, accelerates the dislocation emission by decreasing stacking fault energy and/or elastic modulus, and increases the propensity for planar slip and slip localization at the microscopic scale [5,12–18]. Despite the fact that these conclusions have been drawn from a

large volume of work carried out over decades, the exact mechanism of HE has remained unclear to date. Yet out of several suggestions, including H phase transformation theory [19] and surface pressure theory [20,21], surface energy model [22], brittle crack tip theory [23], only three mechanisms are viable: (i) stress-induced hydride formation and cleavage [24,25], (ii) H-induced decohesion [26,27], and (iii) H-enhanced localized plasticity (HELP) [28–31]. Furthermore, more than one of these HE mechanisms may be simultaneously active, and the dominant one is dictated mainly by the experimental conditions [7].

Stress-induced hydride formation and cleavage embrittlement, which is a result of formation of hydrides at stress concentration locations and volume dilatation, constitutes one of the most important reasons for failure of systems, in which hydrides are either stable or can be stabilized, such as in zirconium (Zr), titanium (Ti), niobium (Nb), vanadium (V), and their alloys [25,32–35]. H-induced decohesion theory, on the other hand, states that presence of H in solid solution causes weakening of interatomic bonds at the crack tip [27,36–38]. Even though there is not one single mechanism applicable to all metallic materials, since each mechanism has a different share in different fracture modes depending on the material, HELP, which is based on both experimental observations and theoretical calculations, is the most widely used theory for explaining HE [24,39]. Specifically, the H interstitial in host matrix shields elastic interactions between dislocations and obstacles, and thereby brings about the localization of slip bands. This increases the dislocation mobility, which causes more plastic deformation at localized region close to the fracture surface, and decreases the fracture strength [1,38,40]. Therefore, H-induced materials fail at lower stress values when compared to their H-free counterparts as H causes softening at the micro-scale [30].

Several experimental observations have been forwarded which support HELP mechanism in face-centered cubic (FCC) [40], body-centered cubic (BCC) [41] and hexagonal close packed (HCP) [24] systems. Both microstructural parameters, such as grain

size and stability of dislocations, and environmental conditions, such as temperature, strain rate and H content, were considered in the experiments to detect their effects on HE susceptibility [42–45]. For instance, the increase of stacking fault energy, which may be brought about by temperature increase or alloying, was reported to improve the resistance of the material to HE in Fe-Mn-C steels [45,46]. At high temperatures, H is located at grain boundaries and/or inclusion-matrix interfaces, facilitated by the additional thermal energy, and interacts with carbides to produce methane. This type of H localization is known as H attack and it is not directly related to HE, however; materials previously exposed to H attack at high temperatures, can be affected by HE at low temperatures [47].

While the strain rate effect on HE can only be observed at moderate strain rates that allow for the H to interact with the dislocations, the dislocation velocity is too large for inducing considerable H segregation at relatively high strain rates [48]. As for the role of H content on HE, both the yield strength of ductile BCC β -titanium samples and the fracture stress of brittle samples decreased with increasing H content due to the enhancement of the interatomic spacing without any significant interactions with the surrounding atoms, which makes the dislocation nucleation easier [49–51]. Similarly, H charging was reported to decrease the macroscopically measured flow stress of iron (Fe) [1]. On the contrary, high strain rate deformation responses of simple nickel (Ni)-, aluminum (Al)-, and Fe-H media exhibited increased macroscopically-measured flow stresses [46,52,53] and yield strengths [54]. Such contrary results from the literature clearly indicate that exact role of H interstitials and HE mechanism in metallic materials have not been fully understood yet.

Various studies focusing on detrimental effects of H on the mechanical properties of metallic materials have shown that, once H diffuses into material, it is located either at normal interstitial lattice sites (NILS) or trap sites, and it is assumed that the populations are always in equilibrium with each other [55,56]. Several H diffusion analyses were carried out to

calculate both steady state and transient values of H occupancy in NILS and in trap sites along with the corresponding mechanical behavior of the host material [38,55–61]. These analyses also accounted for stress gradients, effective plastic strains and H-induced softening, such that H effects on metals and alloys were simulated at both microstructural level, such as void growth and coalescence [56,62,63], and macroscopic level, such as onset of necking in tension and crack propagation behavior [64,65]. Fatigue crack growth behavior and fatigue life in the presence of H have also been investigated in detail since fatigue type of failure under HE is the most significant problem in maintaining the structural integrity of components [2,12,13]. However, there are limited number of studies which focus on mechanistic understanding of H effect at the micro-scale [66]. Even though a theoretical explanation for the onset of shear localization in the presence of H was provided and related to the H-induced material softening at the micro-scale [39], to the best of the authors' knowledge, a proper treatment of this problem incorporating the effect of HE at the atomistic scale into a crystal plasticity model to predict the macroscopic deformation response in the presence of anisotropy has not been forwarded yet.

The current study was undertaken with the intention of improving the understanding of the role of H interstitials on the overall strain hardening behavior of metallic materials by taking the anisotropy of the host alloy into account. For this purpose, an iterative model was proposed, which considers the lattice as an elastic continuum containing a single edge dislocation and featuring unconstrained boundary conditions without any other external forces acting on it. The model was utilized to calculate the H concentration both at the immediate surroundings of and far from a dislocation, also accounting for the relaxation effect due to the presence of H. Based on the overall H concentration in the alloy, net shear stress induced by H interstitials on single dislocations was calculated throughout the matrix. Keeping

temperature and strain rate constant, H content effects on the HE susceptibility of iron were investigated in detail.

It should be noted that the influence of H interstitial on the mechanical response of polycrystalline materials is generally ignored by conventional crystal plasticity models. This paper presents a physically grounded crystal plasticity formulation that accounts for the influence of microstructural parameters on HE susceptibility. Specifically, the classical Voce type hardening in a Visco-Plastic Self-Consistent (VPSC) model was modified, such that both the anisotropy of the host alloy, and the flow stress contribution that reflects the stress field imposed on the arrested dislocations due to the surrounding rate-dependent solute field can be properly treated. In order to verify the modified VPSC model, the crystal plasticity computations were compared to our experimental findings and previously postulated H effect based constitutive models. Overall, our combined experimental and modified modeling effort reported here provides a venue for incorporating the H effect into crystal plasticity and better understanding the mechanism of HE.

4.2 Experimental Procedures

The material tested in this study is high-purity iron (99.3 wt. % Fe) with a BCC crystal structure. Chemical composition of H-free samples as determined by EDX examination is presented in Table 4. 1. Tensile specimens were prepared in accordance with DIN 50125 standards by turning and milling operations, such that the loading axis of each sample extracted from cylindrical iron bars coincided with the rolling direction. Uniaxial monotonic tensile experiments were carried out on a hydraulic test frame equipped with a digital controller, and at a moderate strain rate of 10^{-4} s^{-1} to promote HE and avoid any strain rate

effects (Figure 4. 1). The experiments were repeated on six companion specimens for each case for the sake of consistency of results.

Table 4. 1 Chemical composition of the initial samples prior to H-diffusion. All contents are in wt. %.

C	Si	P	S	Cr	Ni	Mo	Cu	Fe
0.06	0.11	0.012	0.025	0.06	0.11	0.014	0.3	Balance

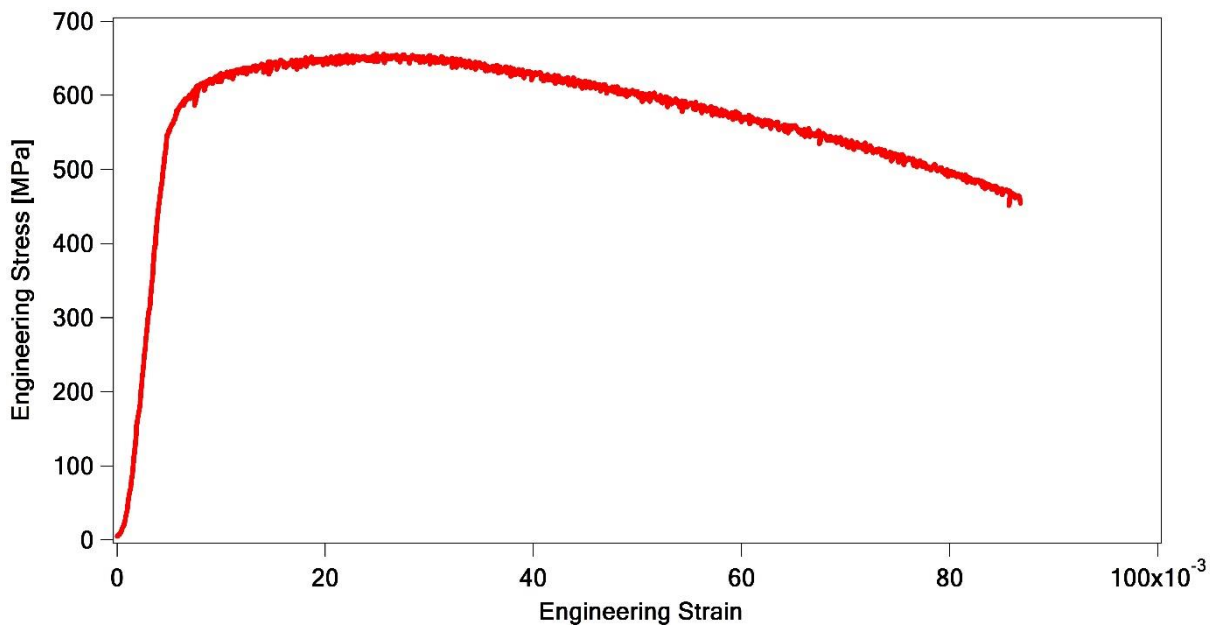


Figure 4. 1 Engineering stress - engineering strain response of hydrogen free sample at room temperature under uniaxial tensile loading and at a strain rate of 1×10^{-4} 1/s. The result shown is the average of three experiments and the test ended with the failure of the specimens.

All samples were characterized by X-ray diffractometer (XRD) (Bruker, D8 Discover, VÅNTEC-500 detector) (Cr tube with $\lambda = 2.291$ Å source, operated at 40 kV and 40 mA) in order to measure residual stresses and texture prior to deformation. XRD profiles were obtained by varying 2θ within 30° - 105° range (Figure 4. 2). The XRD analyses revealed the lack of any significant residual stresses, and therefore, heat treatment was not applied to the tensile test samples to avoid oxidation that may occur during heat treatment process.

Furthermore, the initial texture of the H-free samples (Figure 4. 3) evidenced the presence of an anisotropy corresponding to a Taylor factor of 3.18.

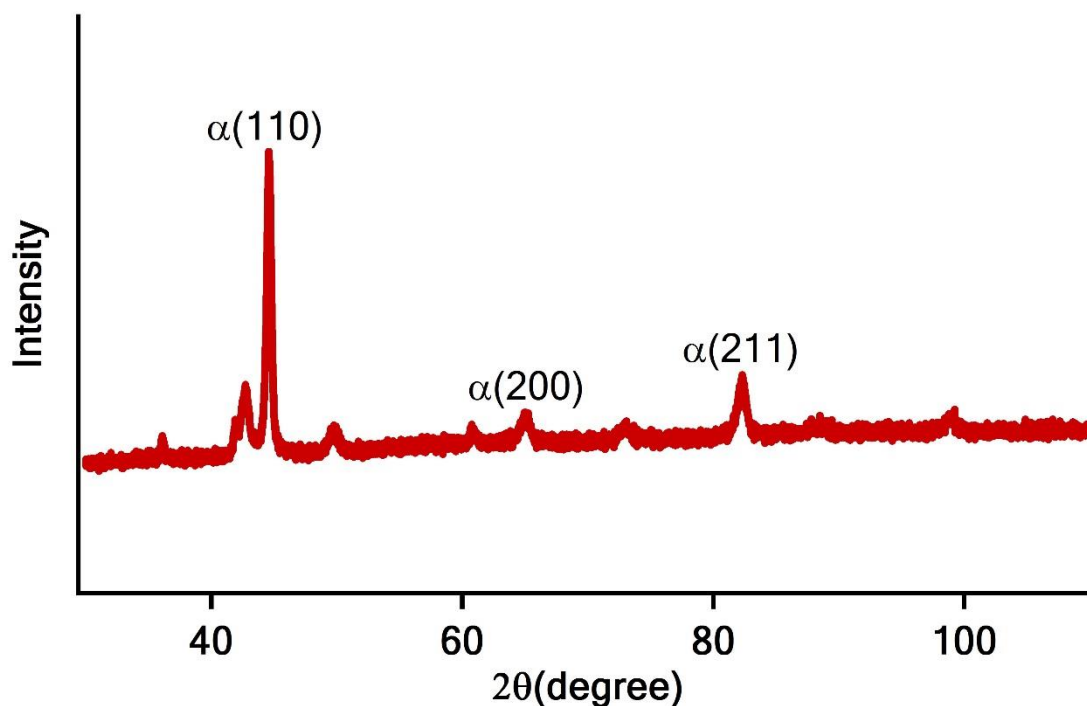


Figure 4. 2 X-ray diffraction pattern of the H-free iron sample.

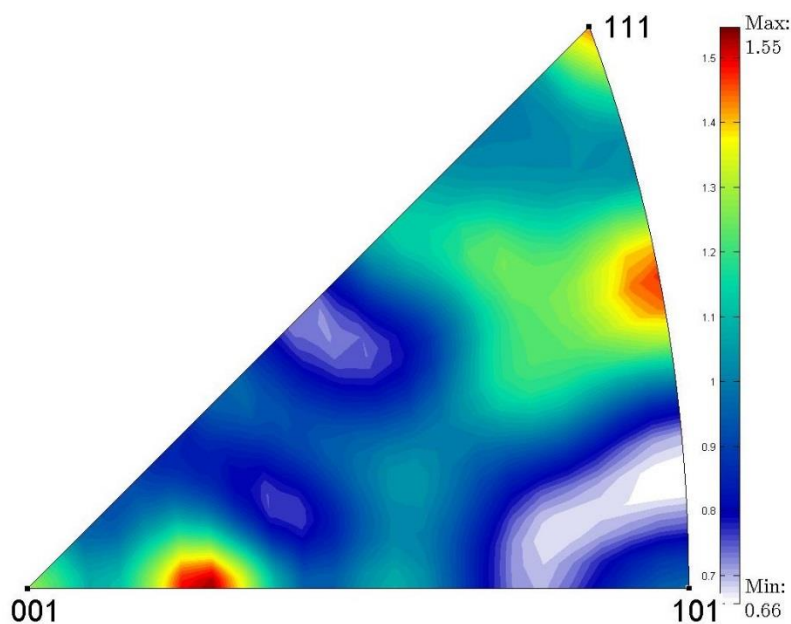


Figure 4. 3 Experimentally measured initial textures of the H-free Fe demonstrating the corresponding degree of anisotropy based on (equal-area projection) inverse pole figure in the direction of tensile loading axis.

All sample surfaces were polished with emery paper before charging with H in order to remove the oxide film. H was introduced into the material before the tension test at room temperature. H charging of specimens was conducted by immersion at open circuit potential in an aqueous solution of 20 mass % Ammonium Thiocyanate (NH₄SCN) for a holding time of 24-120 h. Holding time was adjusted considering the H concentration to reach equilibrium within the whole cross-section of the samples. The amount of H accumulated inside the samples was monitored by H desorption. Prior to experiments, each sample was washed with ethanol and placed into a split tube furnace (Carbolite VST 12/200), where the temperature was increased from 25 to 700 °C and rate of 20 °C/min. Nitrogen gas (99.99% purity) was fed into the furnace with a flow rate of 100 sccm and the exit stream was passed through a heated capillary and analyzed using a mass spectrometer (MKS Cirrus 2 with ionization potential of 70 eV), such that a mass-to-charge ratio of 2 was monitored for quantitative analysis of H.

4.3 Theoretical Considerations

4.3.1 Modeling Transient and Steady-State Solute Concentrations

Effective solute atom concentration, $C(r, \emptyset)$, is a function of the time-dependent solute concentration around a dislocation [67–69]. Accordingly, the time dependent solute atom concentration is expressed as:

$$C(r, \emptyset) = C_m \left\{ 1 - \exp \left[- \left(\frac{C_0}{C_m} \right) (K(r, \emptyset) D t_a)^{\frac{1}{n}} \right] \right\} \quad (1)$$

The term $K(r, \emptyset) D$ is the inverse of characteristic solute diffusion time, t_d , which decreases with plastic straining due to enhanced diffusivity induced by deformation, such that $t_d = (K(r, \emptyset) D)^{-1}$, including the solute-dislocation binding energy, and is inversely proportional to temperature and dislocation density [70]. In Eq. 1 C_m represents the saturation

value of solute concentration at the dislocation core, C_o denotes the initial stress-free alloy solute concentration, and the constant parameter $\bar{n}$ is taken as 2/3 [69,71]. The term t_a represents the aging time, which is the effective time period for which the dislocations are aged, while r and $\emptyset$ are the components of the position vector of H atoms in 2-D polar coordinates relative to the dislocation core. Boltzmann type relaxation effect is included in the equation itself.

Assuming a steady state of motion, the continuity condition requires that $\nabla(C\underline{v}) = 0$, which eventually yields the solute atom concentration as function of position with respect to the dislocation core [61,72,73] :

$$C(r, \emptyset) = \frac{C_o \exp\{-\frac{W^{int}(r, \emptyset)}{kT}\}}{\frac{C_o}{\beta N_L} + [1 - \frac{C_o}{\beta N_L}]} \quad (2)$$

where $\underline{v}$ is the solute atom velocity, W^{int} is the interaction energy, k is Boltzmann's constant, β represents the number of interstitial sites per solvent atom, N_L stands for the number of host atoms per unit lattice volume, and T is absolute temperature (Table 4. 2).

With respect to solute concentration, the velocity of solute atoms relative to dislocations that move in the direction of the unit vector $\underline{i}$ is considered to consist of three components [74]: The drift velocity $\underline{v}_1 = -\frac{D\nabla W^{int}}{kT}$ due to the field of force $-\nabla W^{int}$, diffusion velocity $\underline{v}_2 = -\frac{D\nabla C}{C}$ due to concentration gradients, and a constant velocity $\underline{v}_3 = v\underline{i}$ due to dislocation motion. As a result, velocity of solute atoms relative to dislocations is given by:

$$\underline{v} = \underline{v}_1 + \underline{v}_2 + \underline{v}_3 = -\frac{D\nabla W^{int}}{kT} - \frac{D\nabla C}{C} + v\underline{i} \quad (3)$$

The interaction energy between an atom in substitutional solution and the existing stress field can be defined as [61,75]:

$$W^{int}(r, \varnothing) = -\frac{\sigma_{xx} + \sigma_{yy}}{2} \frac{V_I}{N_A} = \frac{\mu}{2\pi(1-\vartheta)} \left(b \frac{\sin \varnothing}{r} \right) \frac{V_I}{N_A} \quad (4)$$

In Eq. 4, μ , b , ϑ , V_I , N_A represent the Shear modulus, Burgers vector, Poisson's ratio, partial molar volume of the interstitial atom, and Avogadro's number, namely $(6.024) \cdot 10^{23}$ molecules/mole, respectively (Table 4. 2). Volumetric expansion, ∇v due to diffusion of solute atom into solvent matrix is given by the term $\frac{V_I}{N_A}$. Solute atoms' effect on the elastic modulus of the matrix, on the other hand, can be calculated by assigning $c_o = \frac{C_0}{N_L}$ [76]:

$$E = E_0(1 + 0.34c_o), \vartheta = \vartheta_0 - 0.025c_o, \mu = \mu_0 \left(\frac{1+0.34c_o}{1-0.0177c_o} \right) \quad (5)$$

Table 4. 2 The parameters utilized in the current model for the Fe matrix.

μ_0	b	ϑ_0	V_I	β	N_L
86 GPa	0.248 nm	0.29	2.66 x 10⁻⁶	6	0.846 x 10²⁹
			m³/mol		
V_m	v_D	$\dot{\eta}$	G_0	s_{t0}	T
7.11 x 10⁻⁶	1.39 x 10¹³ 1/s	10	0.57 eV	1.04 GPa	298 K
m³/mol					

In order to introduce relaxation effect to steady state interstitial concentration, logarithmic a local concentration model was proposed, which is valid for both close to the dislocation and remote from the dislocation, such that [61]:

$$e^H = \frac{\log(1+c(r,\varnothing)-c_o)\nabla v N_A}{V_M} \quad (6)$$

where V_M represents the molar volume of solvent matrix. Based on this formulation, one can easily calculate the transformation strain and corresponding relaxation stress from the following relationship [61,73,77]:

$$\varepsilon_{ij}^H = \frac{1}{3} e^H \delta_{ij}, \sigma_{ij} = -C_{ijkl} \varepsilon_{kl}^H \quad (7)$$

4.3.2 Computation of the Integrated Shear Stress on a Single Edge Dislocation Imposed by H Interstitials

When dislocation glide is blocked by any obstacle, such as precipitates, solute atoms or microstructural defects, there is an elapse of time before the dislocation overcomes the obstacle. The average time dislocations stay arrested at obstacles throughout the matrix is defined as the waiting time, t_w . The waiting time is proportional to the density of mobile dislocations (ρ_m), the dislocation mean free path (L), and the inverse of the strain rate ($\frac{1}{\dot{\varepsilon}}$). Under steady-state conditions (constant strain rate) the Orowan equation $\dot{\varepsilon} = \rho_m b \bar{v}$ defines the waiting time as $t_w = \frac{\rho_m b L}{\dot{\varepsilon}} = \frac{\Omega}{\dot{\varepsilon}}$ by obeying classical distance-time-velocity formulation where $\bar{v}$ represents the dislocation velocity [68,78–80]. Mean free path of dislocation is inversely proportional to forest dislocation density such that, $L = \frac{1}{\sqrt{\rho_{im}}}$, and thus, the elementary strain, which corresponds to deformation obtained when all mobile dislocations achieve their activation, becomes $\Omega = \frac{\rho_m b}{\sqrt{\rho_{im}}}$ [70,79,81]. The time-dependent average waiting time is a function of fundamental attempt frequency, ν_o , and the energy barrier which depends on the effective resolved shear stress acting on current time, t , [68,70,81]. The attempt frequency depends on mobile dislocation density, burgers vector and the Debye frequency, ν_D , which is a function of both density of the BCC lattice and the speed of sound [82]. Specifically, the average waiting time can be expressed as:

$$t_w = e^{\frac{\Delta G(\tau_{eff}^n)}{kT}} / \nu_o \quad (8)$$

The effective resolved shear stress on slip system n can be formulated as the difference between resolved external stress, τ , and summation of resolved back stress representing the slip system resistance, s_a , and constant thermal stress, τ_a [70,82–84].

$$\tau_{eff}^n = |\tau^n| - s_a^n - \tau_a^n \quad (9)$$

The constitutive law for elastic materials considers the second Piola-Kirchhoff stress tensor T^* , and right the right Cauchy-Green strain tensor, $C^* = F^{*T} F^*$, whereas in isotropic elastic materials Cauchy stress tensor is a function of the left Cauchy-Green strain tensor, $B^* = F^* F^{*T}$. Since elastic stretch can be neglected in metallic materials, τ^n can be expressed as [82,85–87]:

$$\tau^n = (C^* T^*) : s_0^n \cong T^* : s_0^n \quad (10)$$

Resolved back stress comes into picture because of both short-term and long-term dislocation interactions during dislocation motion, and it can be expressed in Taylor hardening format as [82,84,88]:

$$s_a^n = \mu b \sqrt{\sum_{\alpha=1}^n q_p A^n \rho_{total}^n} \quad (11)$$

where q_p refers to the dislocation barrier strength and A^n is the slip system dislocation interaction coefficients matrix.

Even though BCC α -iron can theoretically deform by dislocation glide on 48 slip systems (pencil glide) [89], the {112} and {123} slip planes are not exactly identical to the {110} slip planes in terms of activation energy: slip on {110} slip planes usually during plastic deformation at room temperature or lower temperatures, yet dislocation glide on {123} planes can also be active at very low temperatures (<25 K) [89–92]. Both molecular dynamic and dislocation dynamic simulations assume that $\langle 111 \rangle \{110\}$ slip systems govern the plastic deformation of BCC α -iron is the dominating system to examine atomistic movements

during deformation at all temperature [89,93–95]. Therefore, in our crystal plasticity model, only the $\langle 111 \rangle \{110\}$ slip systems were considered [82]. It should also be noted that effective resolved shear stress on slip system n is assumed to be zero if the summation of resolved back stress and constant thermal stress is greater than resolved external stress [96].

Several energy barrier models were proposed for different types of obstacles by Friedel [97], Estrin and McCormick [69], Kang et al. [98] and Springer [99]. For BCC α -iron the most useful one is Kocks type activation energy equation [82,88,100,101], which can be expressed as:

$$G(\tau_{eff}^n) = G_0 \left[1 - \left(\frac{\tau_{eff}^n}{s_{t0}} \right)^p \right]^q \quad (12)$$

where G_0 is the zero effective shear stress activation energy, p and q are the profiling parameters, and the constant s_{t0} represents the thermal slip resistance at 0 K (Peierls stress) [82]. In order to calculate BCC α -iron activation parameters, the Nudged Elastic Band (NEB) method was used by Narayanan et al [82]. Moreover, using effective stress dependent activation energy dislocation velocity on slip α system can be modeled as:

$$v^n = v_0 e^{-\Delta G(\tau_{eff}^n)/kT} \quad (13)$$

Shear rate on slip system n can be calculated combining Eq. 13 with the Orowan equation [82,84,102,103]:

$$\dot{\varepsilon}^n = \dot{\varepsilon}_0 \left(\frac{\tau_{eff}^n}{s_{t0}} \right)^{\dot{\eta}} e^{-\frac{\Delta G(\tau_{eff}^n)}{kT}} \text{sign}(\tau_{eff}^n) \quad (14)$$

where material parameters $\dot{\varepsilon}_0$ and $\dot{\eta}$ stand for the reference strain rate and the inverse of the rate sensitivity index, respectively.

It was previously shown that the effective aging time of the dislocations, t_a , by the solute atoms pinning them is less than the waiting time, t_w , and therefore t_a is used to establish the time dependency of the solute atom concentration. Accordingly, the non-steady-state aging time relates to waiting time as [68,70,71,80,104]:

$$\frac{dt_a}{dt} = 1 - \frac{t_a}{t_w} \quad (15)$$

Impurities can act as obstacles against dislocation glide at very high temperatures, which ensures more energy to the system. At the prior stages of deformation, since a high density of forest dislocations are not activate yet, $\frac{dt_a}{dt} \cong 1$, as in static strain aging. As the deformation advances within the plastic regime and as the plastic strain rate increases, rate of change of the aging time becomes negative, that is $\frac{dt_a}{dt} < 0$ [79]. Similarly, the more both dislocation density and solute diffusion coefficient increase, the less the aging time will be [105]. Considering the definition of the waiting time given by the Orowan equation, i.e. the aging time is a function of strain and strain rate history, the time dependence of aging time determines the transient behavior of the solute concentration, $C(r, \phi)$, based on Eq. 1. Additionally, aging time will be equal to waiting time, i.e $t_a = t_w$, only for steady state conditions [71]. In the current model, the transient response of aging time was successfully modeled by solving first-order kinetic model at all waiting times.

The influence of H is modeled by a continuous distribution of dilatation lines whose strength depends on the local solvent concentration around arrested edge dislocations. Accordingly, the shear stress, τ_H , imposed on a positive edge dislocation due to the surrounding solute atom concentration is given by [61]:

$$\tau_H = -\frac{\mu}{2\pi(1-\nu)} \frac{V_H}{N_A} \int_0^{2\pi} \int_{r_i}^{r_o} C(r, \phi) \frac{\sin 2\phi}{r} dr d\phi \quad (16)$$

The inner and outer cut-off radii of the H atmosphere surrounding the edge dislocation are given by r_i and r_o , respectively and. It should be noted that the interaction energy is not valid at $r_i = 0$ since the elastic continuum theory is not applicable at the origin. Therefore, $r_i = b$ and $r_o = 10b$ are assigned as the integration limits for Eq. 16. The shear stress, τ_H , represents the additional shear stress on a single edge dislocation due to the surrounding

solute atom concentration. The constants utilized in the current model are presented in Table 4. 2.

4.3.3 Computation of Diffusion Time and Dislocation Density

The component $K(r, \emptyset)D$ in Eq. 1 is the diffusion time, t_d , and can also be expressed as [70]:

$$t_d = \frac{t_{d0}}{\rho_t} \exp\left(\frac{\Delta G(\tau_{eff}^n)}{kT}\right) \quad (17)$$

where ρ_t is total dislocation density and t_{d0} is the pre-exponential factor which can be considered constant. The total dislocation density consists of geometrically necessary dislocations (GNDs) which is the minimum dislocation density to accommodate a given strain gradient, statistically stored dislocations (SSDs) which contribute to plastic straining, and grain boundary dislocations (GBD) which account for lattice incompatibilities across grain boundaries:

$$\rho_{total}^k = \rho_{GND}^k + \rho_{SSD}^k + \rho_{GBD}^k \quad (18)$$

GNDs preserve lattice continuity by causing local lattice curvature while accommodating strain gradients. Random trapping process of mobile dislocations is the source of SSDs which causes crystallographic slip on the distinct slip planes. The GBDs, on the other hand, are the interacted dislocations between dislocations and grain boundaries. They can either be glide-type which lie on the grain boundaries, or climb-type which glide out of grain boundary planes [106–108]. The effect of grain boundary dislocations were ignored in the current modeling effort.

The grain boundary type plays crucial role for GBDs. In recent years, atomistic simulations and crystal plasticity finite element (CPFE) models have been carried out to account for GBD effects on heterogeneous plastic deformation. However, it is a very

challenging problem to incorporate the GBDs atomic formulations into meso-scale models [106,109–112]. Several studies pointed out that GNDs have similar significance to GBD, and thus, edge GNDs assumed to also represent the GBDs [108]. In Eq. 18 different approaches were used to superpose dislocation densities to calculate the total dislocation density. For instance, Flech et al. chose $k=2$, while another model was constructed taking $k<1$ [113,114]. In the current study, k is taken as 1 to ensure geometrical considerations. It should be noted that for k values different than 1, GNDs effect on flow stress was shown to be minor [115,116].

Since a crystal is distorted by GNDs there will be some angle β between sides of lattice and spacing d between parallel slip planes. Dividing β to d gives plastic strain gradient η^p . Estimation of GNDs can be expressed as for small angle assumption ($\beta = b/d$) [116]:

$$\rho_{GND} = \frac{1}{d^2} = \frac{\eta^p}{b} \quad (19)$$

Equivalent plastic strain, $\bar{\epsilon}^p = \frac{b}{d} = \sqrt{\frac{1}{2} \epsilon_{ij}^p \epsilon_{ij}^p} = \frac{1}{\sqrt{3}} \gamma$ from classical mechanics can be utilized for taking the SSDs into account since they are produced during deformation. General formulation of the SSD density is [116] :

$$\rho_{SSD} = \frac{1}{ld} \quad (20)$$

where l is travel distance of dislocation segment whose magnetite is calculated experimentally and $\gamma = \frac{b}{d}$ is plastic shear. Combining the definitions of SSD density and equivalent plastic strain leads us to [116]:

$$\rho_{SSD} = \frac{\sqrt{3} \bar{\epsilon}^p}{lb} \quad (21)$$

4.3.4 Modeling of Slip-Dominant Deformation Behavior in the Presence of H Interstitials

The modified VPSC algorithm utilized in this study accounts for the deformation in the plastic zone only, and considers the plastic deformation to take place when one or more slip or twinning systems become active. The classical Voce hardening scheme [117] is utilized to define the work hardening of the material, such that the microscopic flow stress is updated for each increment according to the following equation:

$$\dot{\tau} = \sum_n \left\{ \theta_0 \left(\frac{\tau_s - \tau}{\tau_s - \tau_0} \right) \right\} |\dot{\gamma}^n| \quad (22)$$

where θ_0 is the constant strain hardening rate and τ_0 is the reference strength, which is usually taken as the initial microscopic yield strength calculated based on the experimental macroscopic yield strength [118]. The term τ_s represents the saturation stress in the absence of geometric effects, or the threshold stress, while the shear strain rate of the n^{th} active system is represented by $\dot{\gamma}^n$. The hardening can be defined by an extended Voce law [118], which is characterized by the evolution of the threshold stress, τ^s , with accumulated shear strain (Γ) in each grain:

$$\tau^s = \tau_0 + (\tau_1 + \theta_1 \Gamma) \left(1 - \exp \left(- \frac{\theta_0 \Gamma}{\tau_1} \right) \right) \quad (23)$$

where τ_0 is the reference strength, and τ_1 , θ_0 and θ_1 are the parameters that define the hardening behavior. The hardening law defined by Eq. 23 characterizes the onset of plasticity and the saturation of threshold stress at larger strains.

To be able to account for the solute effect on the flow strain, we consider the quantity given by Eq. 24 as an average value throughout each grain. Then, the classical Voce

hardening scheme is further modified to account for the solute effect, such that the rate of flow stress becomes:

$$\dot{\tau} = \sum_n \left\{ \theta_0 \left(\frac{\tau_s - \tau}{\tau_s - \tau_0} \right) \right\} |\dot{\gamma}^n| + M_i S \frac{d\tau_H}{dt} \quad (24)$$

where $M_i = d\sigma_i/d\ln\dot{\epsilon}$ is the instantaneous strain rate sensitivity that takes into account the abrupt strain rate changes and instantaneous changes in flow stress during deformation, and S is the scaling factor that reflects the contribution to hardening throughout the whole grain. The term $\frac{d\tau_H}{dt}$ obtained by the differentiation of τ_H , given in Eq. 24 with respect to time and substitution of Eq.s 1 and 15.

$$\frac{d\tau_H}{dt} = -\frac{\mu}{2\pi(1-\nu)} \frac{V_H}{N_A} \int_0^{2\pi} \int_{r_i}^{r_o} \frac{2C_0[K(r,\phi)D]^{\frac{2}{3}} \exp\left[-\left(\frac{C_0}{C_m}\right)(K(r,\phi)Dt_a)^{\frac{2}{3}}\right]}{3t_a^{\frac{1}{3}}} \left(1 - \frac{t_a}{t_w}\right) \frac{\sin 2\phi}{r} dr d\phi \quad (25)$$

In its extended form, the modified Voce hardening rule can be obtained from Eq.s 23, 24 and 25 as in the following expression:

$$\tau_s = \tau_0 + (\tau_1 + \theta_1 \Gamma)(1 - \exp\left(-\frac{\theta_0 \Gamma}{\tau_1}\right)) - S \frac{\mu}{2\pi(1-\nu)} \frac{V_H}{N_A} \int_0^{2\pi} \int_{r_i}^{r_o} \frac{2C_0[K(r,\phi)D]^{\frac{2}{3}} \exp\left[-\left(\frac{C_0}{C_m}\right)(K(r,\phi)Dt_a)^{\frac{2}{3}}\right]}{3t_a^{\frac{1}{3}}} \left(1 - \frac{t_a}{t_w}\right) \frac{\sin 2\phi}{r} dr d\phi \quad (26)$$

Consequently, the classical Voce hardening scheme in Eq. 22 was modified by taking into consideration the additional contributions of H atoms to hardening as presented in Eq. 26. The experimentally determined initial textures of iron and H-alloyed iron samples were incorporated into the modified VPSC model described by Eq. 26 to predict the macroscopic deformation response of each material under uniaxial tensile loading.

4.4 Results and Discussion

Uniaxial tensile tests were carried out to observe the effect of H at macroscopic level at a moderate strain rate of 10^{-4} 1/s, which is low enough to promote HE with simultaneous reduction in area by allowing the sweep of H by dislocations. The experimental stress-strain curves of H-diffused and H-free samples are shown in Figure 4. 4. The elastic behaviors of the samples are quite the same, and the serrations in the flow curves increase with increasing H content in the samples at room temperature. The loss in ductility of the H-induced samples varies between 30-37% as compared to the deformation response of the H-free sample. This significant decrease of the ductility with increasing H content can be explained with the HELP mechanism, which suggests that H in the metallic matrix decreases the barriers against dislocation motion and increases the amount of deformation in a localized region near the fracture surface [38,40,119]. The observed decrease of ductility due to H agrees well with previous works [34,120]. Moreover, H slightly decreases the stresses attained throughout the plastic deformation zone (Figure 4. 4), which is brought about by the H-dislocation interactions. Specifically, H shields dislocations from interacting with other obstacles, which promotes dislocation motion at lower stresses [49,121]. Decrease in the local stress values is directly proportional to H concentration, which indicates that the HE susceptibility increases with H concentration. This finding stands in good agreement with previous studies [11,122,123]. The decrease in the ultimate tensile strength and work hardening rate of the samples with H concentration can be also clearly observed in Figure 4. 4.

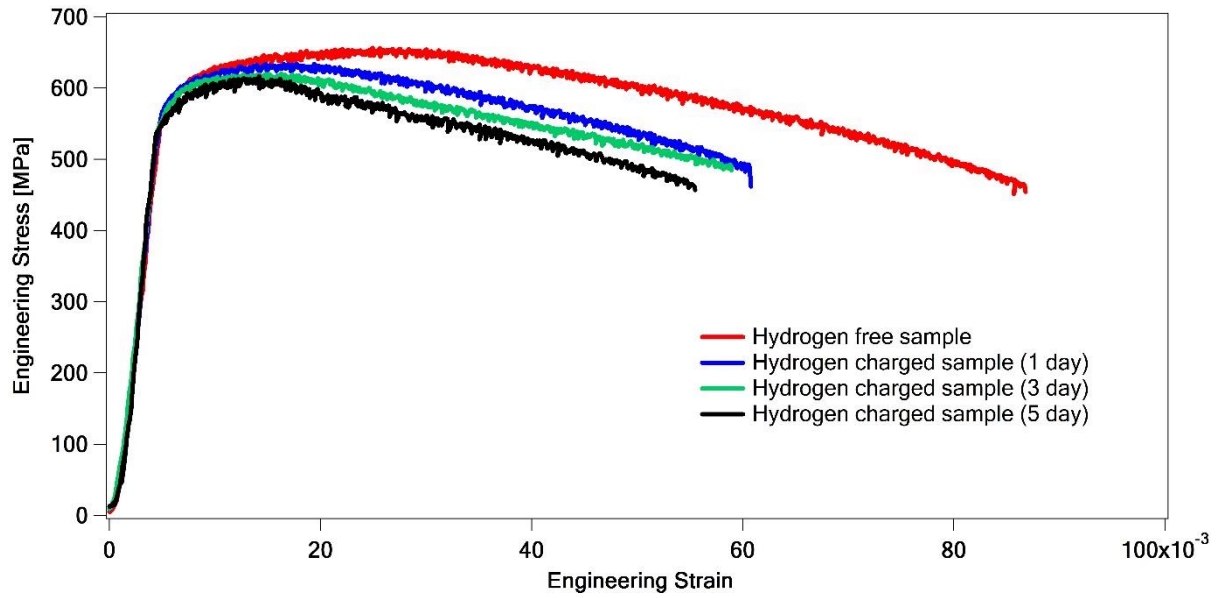


Figure 4. 4 The room temperature uniaxial tensile deformation response of as-received and H-charged specimens at a strain rate of 1×10^{-4} 1/s.

Both H-free and H-induced samples exhibit cup-cone ruptures characterized by a microvoid coalescence upon fracture, and dimpled fracture mode is observed (Figure 4. 5). Thus, fracture modes of both samples are ductile and are not effected by H charging, which was also forwarded in the work by Tiwari et al. [9], where electrolytic charged steels were strained up to fracture at a strain rate of 3×10^{-5} 1/s under uniaxial loading conditions. On the other hand, H-enhanced decohesion mechanism states that sufficiently high H concentration in metals changes the fracture mode from ductile to brittle, which was observed in previous studies [49,124,125], as well.

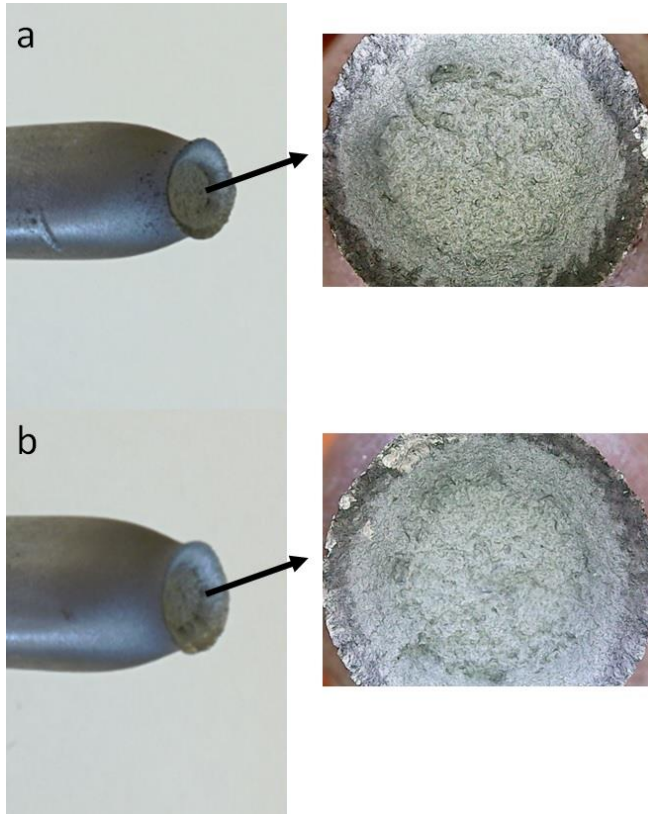


Figure 4. 5 Fracture surfaces of the (a) as-received and (b) H-charged specimens.

Even though a few studies were carried out to address the critical question of how H-induced material softening at micro-scale promotes shear localization at the macroscale [39,63], to the best of the authors' knowledge, a thorough crystal plasticity modeling effort incorporating the H effect on the hardening response of the metallic materials has not been forwarded yet. It has been concluded that macroscopic material response modeling can be achieved by proper micro-scale modeling based on experimental data obtained from basic modes of loading, such as the uniaxial tensile loading [126]. In the current study, H effect on iron's mechanical response at micro-scale was modeled successfully and the macroscopic deformation responses of H-induced samples were predicted by proper implementation of H-induced shear strain into a classical crystal plasticity formulation. Specifically, a numerical model was proposed to account for the mechanical effects of stress relaxation induced by H and incorporate the atomistically-informed shear strains due to H interstitials into the classical

VPSC formulation at microscopic scale, along with the experimentally measured initial textures of undeformed samples.

Assuming the initial local H concentration as 0.1 H per solvent atom, an iterative model was utilized to compute H-induced relaxation effect and H concentration around dislocation until the error in normalized H distribution converges to 10^{-5} using steady-state solute concentration modeling theory. H-induced relaxation trends for positive and negative burger vectors are demonstrated in Figure 4. 6. The volumetric strain and corresponding relaxation stresses proposed in a previous study [73] was modified in the current study along with Eq. 7. The relaxation effect, which is more pronounced at the vicinity of a dislocation, based on the normalized H concentration can be observed in Figure 4. 7. The model accurately predicts the H concentration both close to and remote from a dislocation taking into account the relaxation effect. It is obvious that solute concentration lines map the contours of hydrostatic stresses around a dislocation. Our model corresponds well with the previously calculated H distribution contours around single edge dislocation with different types of host matrices and environmental conditions [34,61,73].

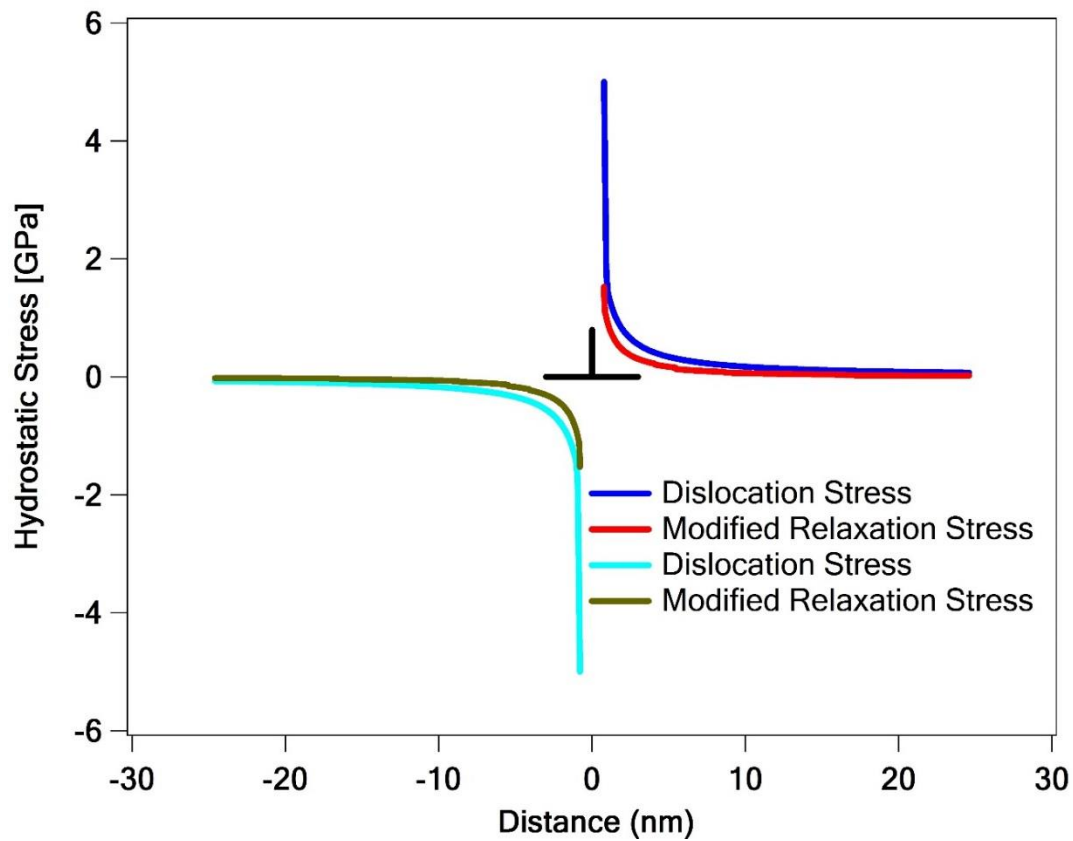


Figure 4. 6 H-induced relaxation stress and hydrostatic stress as a function of distance from the core of an edge dislocation.

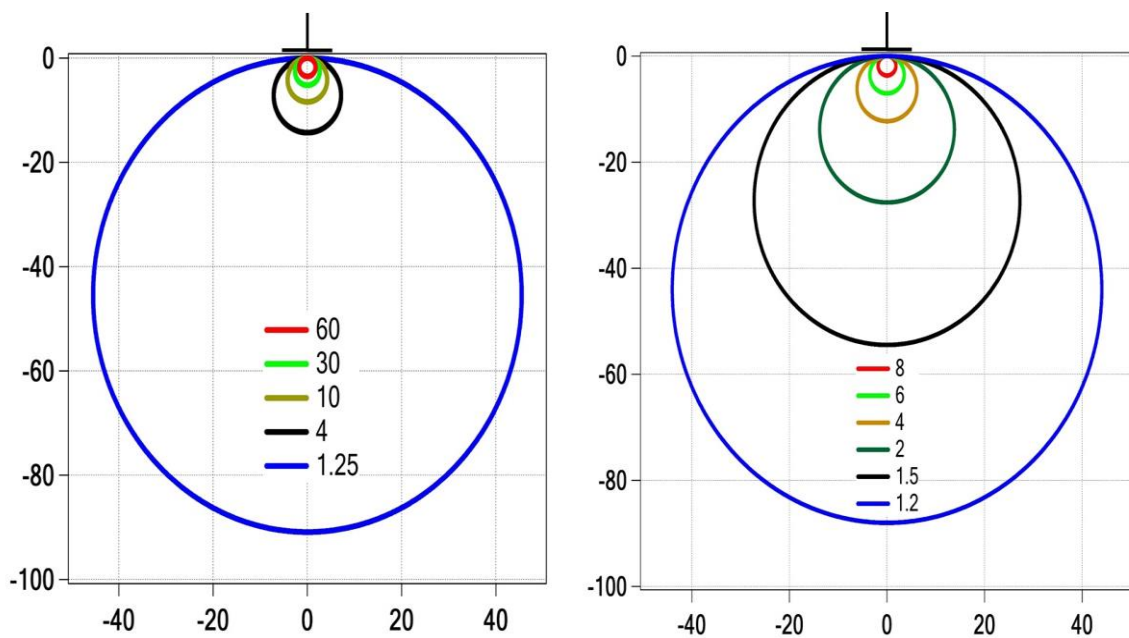


Figure 4. 7 Contours of initial and post-relaxation H concentration surrounding a single edge dislocation in Fe matrix.

The time-dependent H concentration modeling was carried out to incorporate the atomistically-informed shear strain due to H interstitial into the classical VPSC formulation. H concentration calculations for different immersion periods (Figure 4. 8), were carried out by H desorption coupled with mass spectrometry for initial stress-free solute atom concentration in Eq.1. Similar H desorption rate profiles were obtained for samples with different immersion periods, as shown in Figure 4. 8. The shift to higher values of peak point temperatures with increasing immersion times indicates an increase in binding energy of adsorbed H, and thus, the adsorption strength. Since the cathodic reaction, which involves the decomposition of SCN^- ions (Eq.27), was observed to continue throughout the whole immersion period and contribute to the increase in the H content [127], one can presume that the fraction of adsorbed gas with higher binding energies increased with the enhanced H adsorption due to the SCN^- decomposition. In other words, higher exposure times enabled H capture to higher binding energy sites:

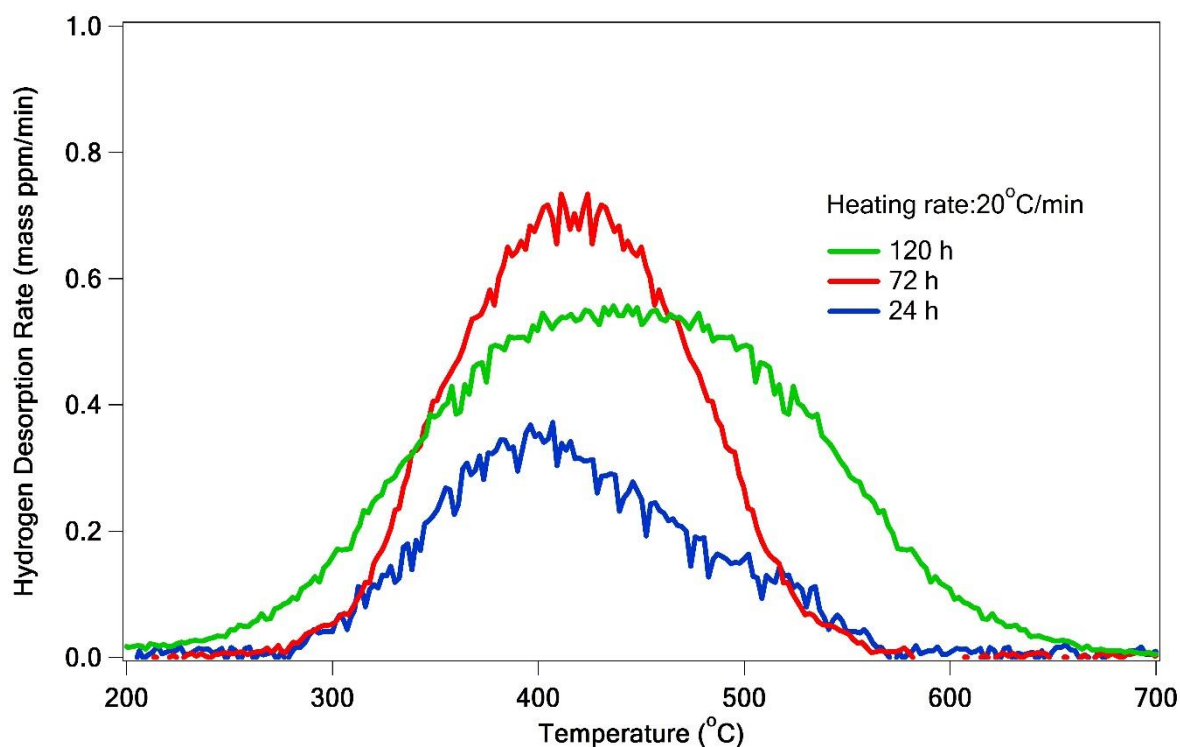
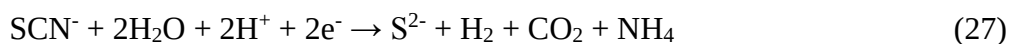


Figure 4. 8 H desorption rate profiles of samples with different immersion times.

The profile of 120 h immersed sample, on the other hand, is broader hence it clues different types of adsorption interactions. Such profile could be obtained due to a possible multilayer adsorption with increasing H content, in which H molecules adsorbed on top of each other might have emerged at relatively lower temperatures and strongly adsorbed ones to the high binding energy sites of iron might be the reason for the elevated temperature evolution rates. Emergence of high temperature H signal in Figure 4. 8 for the 120 h immersed sample can be associated with the fact that longer immersion time leads to higher portions of adsorbed H to diffuse through the iron core, which get trapped effectively by the natural interstitial lattice sites, dislocations, and inclusions [128]. The total amount trapped H content for each sample was calculated from the area underneath the H desorption curves and plotted in Figure 4. 9. Accordingly, 2.94, 5.12 and 6.07 mass ppm of H was adsorbed by the 24 h, 72 h and 120 h immersed samples, respectively. Moreover, the rate of increase in H content with immersion time declined for the experimental time period of 120 h. This finding was attributed to a generation of FeS corrosion film, which decreases the rate of SCN^- decomposition, as demonstrated by several studies [127,128]. Both mass transfer deterioration due to the lowered concentration gradient and corrosion effects might be the cause of such decrease in the slope, since the increase in H content was sustained for all immersion periods which implies the superior adsorption rate to the desorption of H.

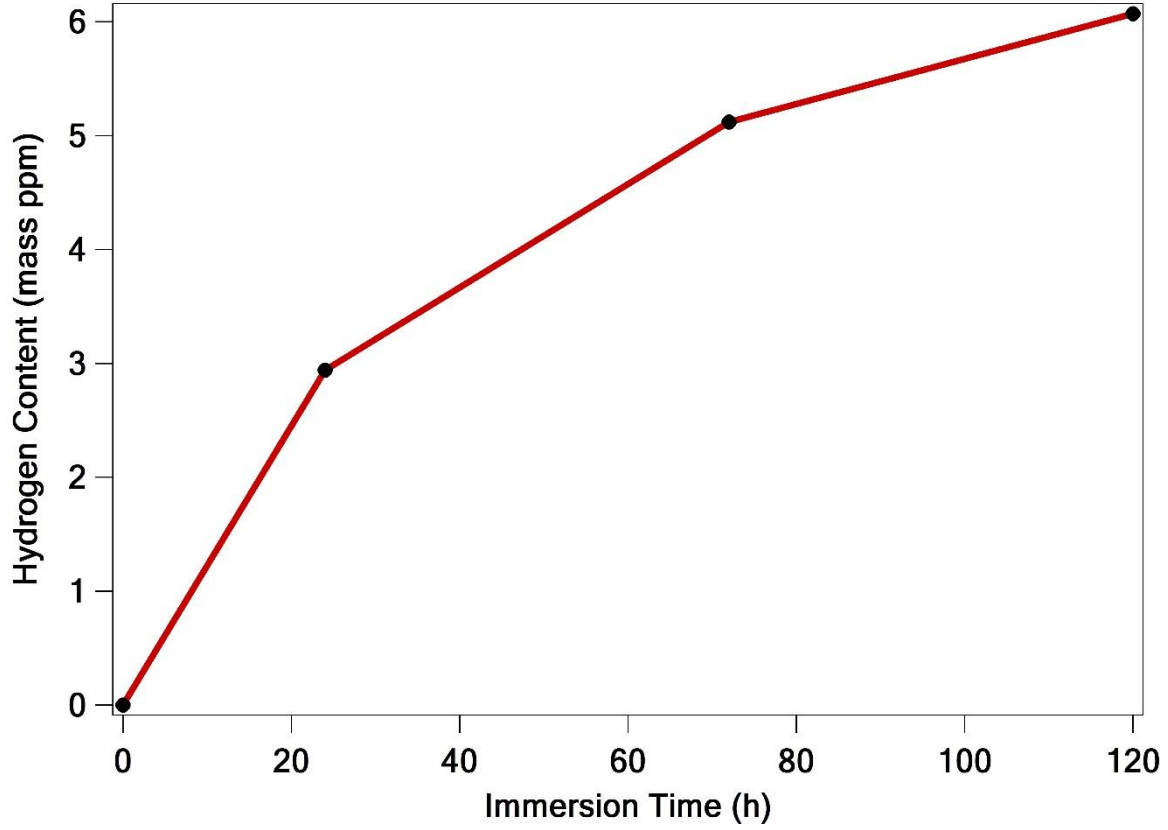


Figure 4. 9 Change of hydrogen content with immersion time.

In addition to H content determination, energy barrier model should also be constructed for the calculation of the waiting time and the corresponding aging time to model time dependent H concentration. In the literature, the molecular static and dynamic simulations and experiments were performed to obtain energy barrier parameters for BCC Fe matrix in Eq. 12. For instance, Koester et al. utilized $p = 1$ and $q = 2$ [101], and Yalcinkaya et al. chose $p = 1$ and $q = 1$ for their atomistically-informed crystal plasticity models [129]. Moreover, based on experimental results, Tang et al. determined $p=0.748$, $q= 1.172$ for BCC Tantalum (Ta). Nevertheless, the most convenient energy barrier parameters for Fe were proposed by Narayanan et al [82], such that the corresponding parameters were chosen as $G_0 = 0.57$ eV, $s_{t0} = 1.04$ GPa, $p=0.67$ and $q=1.18$ in our model (Figure 4. 10). It is evident from Figure 4. 10 that, E_0 is the upper limit of y-axis and s_{t0} is the max limit of the x-axis. In

activation energy calculation equation (Eq.12), which includes non-Schmid effects, Fe is assumed not to show any crystallographic asymmetry effects.

Effective shear stresses were calculated at each deformation step utilizing Eq. 9. Using these effective stresses and corresponding activation energy values, the average waiting time in Eq. 8 was estimated. According to Eq. 8, the amount of strain hardening by H decreases with attempt frequency since the waiting time is inversely proportional to attempt frequency. Steady state and non-steady state aging times were calculated solving the Eq. 15. The non-steady state behavior of aging time with respect to waiting time is shown in Figure 4. 11.

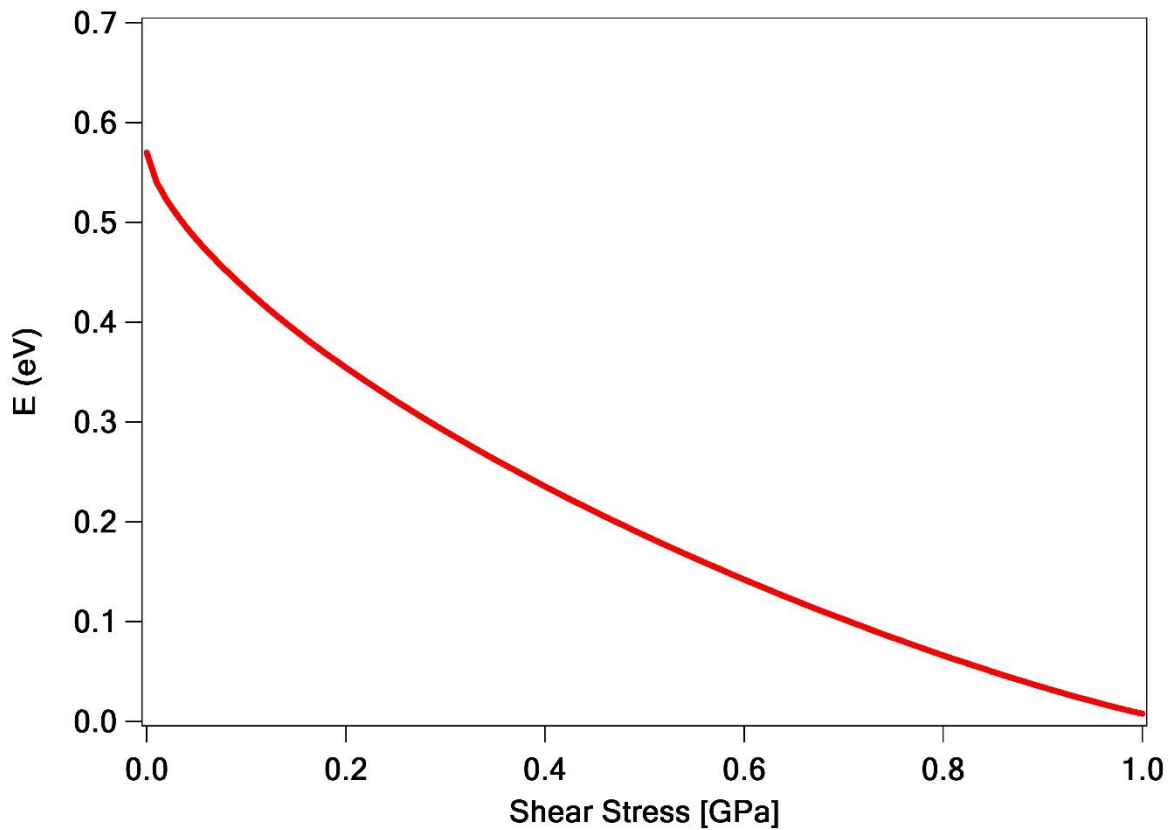


Figure 4. 10 Shear stress dependence of activation energy [82].

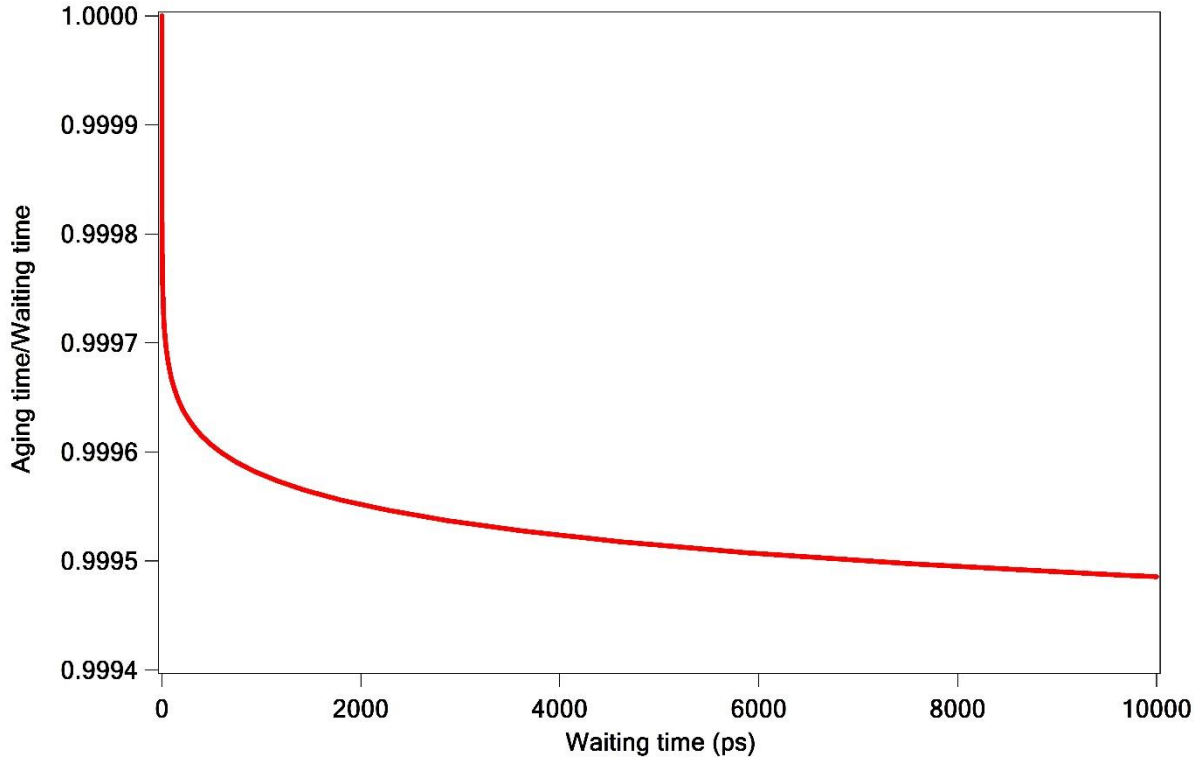


Figure 4. 11 Waiting time – aging time relationship utilized in the current model. The plot shows aging time as a function of waiting time in normalized fashion.

In order to take the integral of Eq. 16, Taylor expansion of $\mathcal{C}(r, \emptyset)$ at constant $\emptyset$ and $r=0$ was taken since there is a singularity at this point. Utilizing the 40×40 Gaussian quadrature rule, which is a weighted sum of function values at specified points within the domain of integration, such that $\sum_{i=1}^n w_i f(x_i)$, the shear stress induced by H was obtained. Points, x_i s and weights, w_i s for inner and outer integrals for $c_0 = 0.1$ are provided in Table 4. 3, and the corresponding shear stress distribution as function of distance from the dislocation core due to H interstitials is represented in Figure 4. 12 with different representative c_0 values at room temperature. Accordingly, the magnitude of shear stress against an edge dislocation increases with increasing nominal H concentration, which result is in a good agreement with the previous results [34,61].

Table 4. 3 Points and weights for inner and outer integrals.

Inner		Outer	
xi	wi	xi	wi
2.48E-09	5.04E-12	6.27765	0.01420
2.47E-09	1.171E-11	6.25405	0.03298
2.45E-09	1.831E-11	6.21175	0.05159
2.43E-09	2.481E-11	6.15098	0.06989
2.40E-09	3.115E-11	6.07211	0.08777
2.37E-09	3.731E-11	5.97562	0.10512
2.33E-09	4.325E-11	5.86208	0.12184
2.28E-09	4.892E-11	5.73219	0.13782
2.23E-09	5.43E-11	5.58671	0.15298
2.17E-09	5.935E-11	5.42653	0.16722
2.11E-09	6.405E-11	5.25261	0.18045
2.05E-09	6.836E-11	5.06599	0.19260
1.98E-09	7.226E-11	4.86779	0.20359
1.90E-09	7.573E-11	4.65922	0.21335
1.82E-09	7.874E-11	4.44152	0.22183
1.74E-09	8.128E-11	4.21600	0.22898
1.66E-09	8.332E-11	3.98402	0.23475
1.58E-09	8.487E-11	3.74697	0.23911
1.49E-09	8.591E-11	3.50628	0.24203
1.41E-09	8.643E-11	3.26340	0.24349
1.32E-09	8.643E-11	3.01979	0.24349
1.23E-09	8.591E-11	2.77690	0.24203
1.15E-09	8.487E-11	2.53622	0.23911
1.06E-09	8.332E-11	2.29917	0.23475
9.82E-10	8.128E-11	2.06719	0.22898
9.01E-10	7.874E-11	1.84167	0.22183
8.24E-10	7.573E-11	1.62397	0.21335

7.50E-10	7.226E-11	1.41539	0.20359
6.80E-10	6.836E-11	1.21720	0.19260
6.14E-10	6.405E-11	1.03058	0.18045
5.52E-10	5.935E-11	0.85665	0.16722
4.95E-10	5.43E-11	0.69647	0.15298
4.43E-10	4.892E-11	0.55100	0.13782
3.97E-10	4.325E-11	0.42110	0.12184
3.57E-10	3.731E-11	0.30757	0.10512
3.23E-10	3.115E-11	0.21107	0.08777
2.95E-10	2.481E-11	0.13221	0.06989
2.73E-10	1.831E-11	0.07144	0.05159
2.58E-10	1.171E-11	0.02913	0.03298
2.50E-10	5.04E-12	0.00554	0.01420

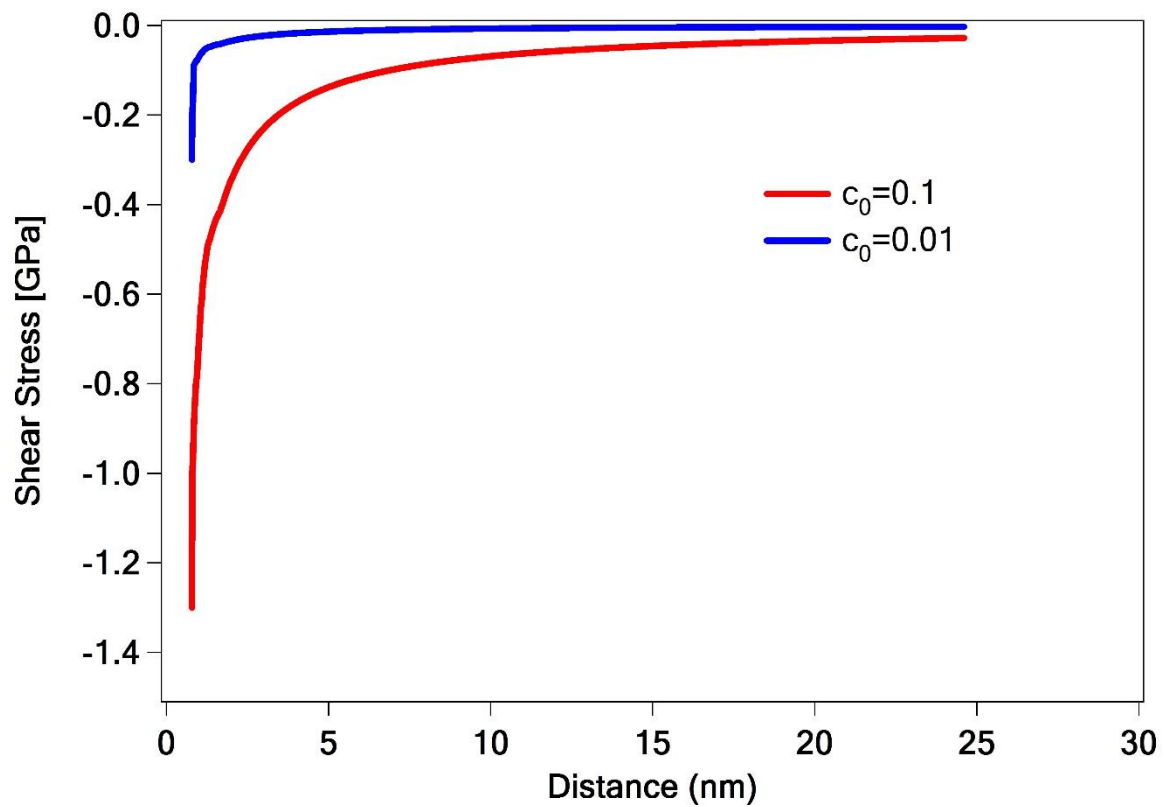


Figure 4. 12 H-induced shear stress in Fe matrix for 0.1 and 0.01 at. % nominal H concentrations.

Using this theoretical foundation, a unique work hardening model that was detailed in Section 3 was proposed by modifying the critical shear stress on the slip systems with respect to measured H concentration to predict the strain hardening response of H-induced polycrystals under tensile loading. For this purpose, standard VPSC simulations [130] were conducted to predict the microscopic deformation response of H-free samples at a strain rate of 10^{-4} 1/s. A comparison between the classical VPSC simulation and the modified VPSC simulations, which were carried out by introducing the new hardening model into the classical Voce hardening scheme, clearly demonstrated the H effect on the overall material response from a theoretical point of view. Specifically, the classical Voce type hardening scheme was modified by accounting the H interstitial effect at the micro-scale through Eq. 26. Plastic deformation behaviors of H-free and (Figure 4. 13) H-induced samples were modeled until necking (Figures 4. 14 - 4. 16) since VPSC considers only the homogeneous portion of the plastic deformation. Experimentally measured initial textures were utilized as an input and allowed to evolve with deformation in order to introduce anisotropy effects into the model. The simulation results agree well with the experimental responses, which demonstrate the success of our multi-scale model.

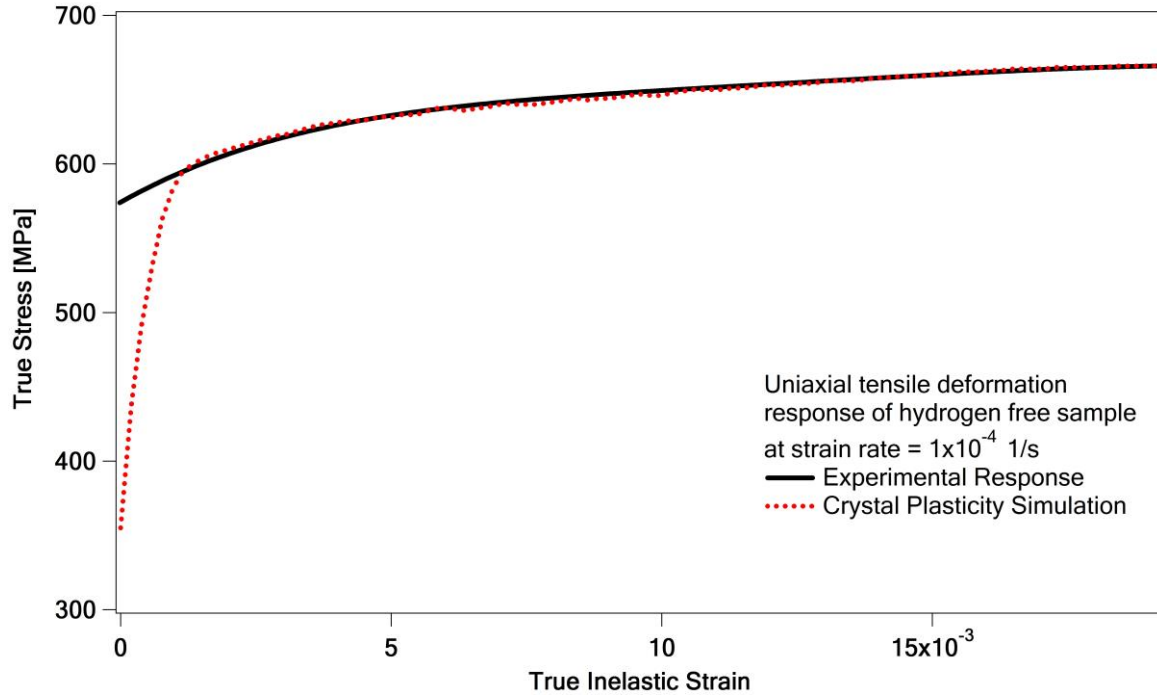


Figure 4. 13 Crystal plasticity simulation of the uniaxial tensile deformation response of the H-free sample at a strain rate of 1×10^{-4} 1/s presented in comparison with the corresponding experimental result.

The initial set of crystal plasticity computations were carried out without taking into account the H-induced shear stress effect (Figure 4. 13). The hardening parameters, which are $\tau_0 = 179.04$ MPa (based on Taylor analyses), $\tau_1 = 159.7$ MPa, $\theta_0 = 100750$ MPa, $\theta_1 = 559.4$ MPa, were utilized to predict the deformation response of the H-free samples. The same hardening parameters, which were determined through a step-by-step procedure based on a secant type inclusion-matrix interaction, were adopted in the simulations of the deformation behavior of H-induced samples, as well. The additional shear strain rate terms due to the introduction of H were calculated and incorporated into the crystal plasticity computations through Eq.s 1-26 with the corresponding H contents. Following the same hardening trend in modified VPSC simulations was provided with the aid of using the same Voce hardening parameters with classical VPSC simulation and contribution of H effect on the hardening response was observed. The scaling factor S of the Eq. 26 was determined as 1.07, 1.12 and 1.28 for the 1-day immersed sample, the 3-day immersed sample and the 5-day immersed

sample, respectively. It can be realized that, the tensile deformation responses of H-induced samples were predicted smoothly via crystal plasticity by incorporation of H-induced shear strain rate. This is an indication of the fact that the Voce hardening parameters do not change the contribution of H effect to the overall hardening, and the corresponding simulation results clearly demonstrate the necessity of the incorporation of H interstitial effect into the crystal plasticity model in order to predict the macroscopic deformation response of H-induced samples.

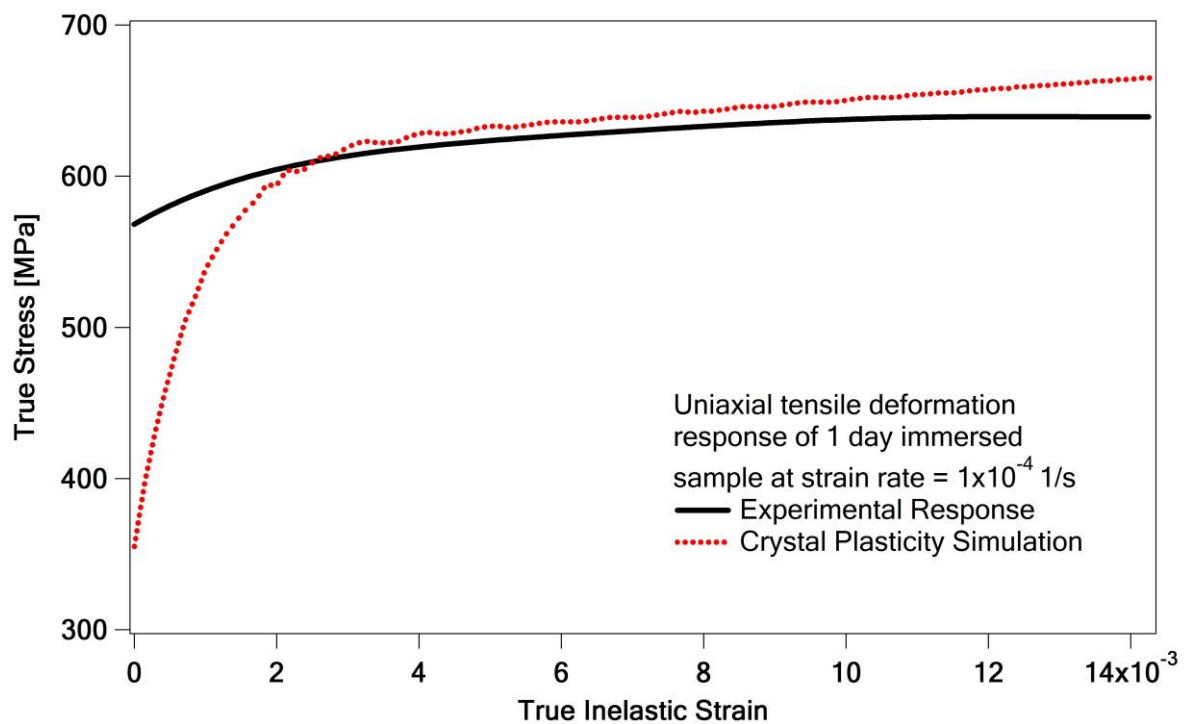


Figure 4. 14 Crystal plasticity simulation of the uniaxial tensile deformation response of the H-charged sample immersed for 1 day at a strain rate of 1×10^{-4} 1/s presented in comparison with the corresponding experimental result.

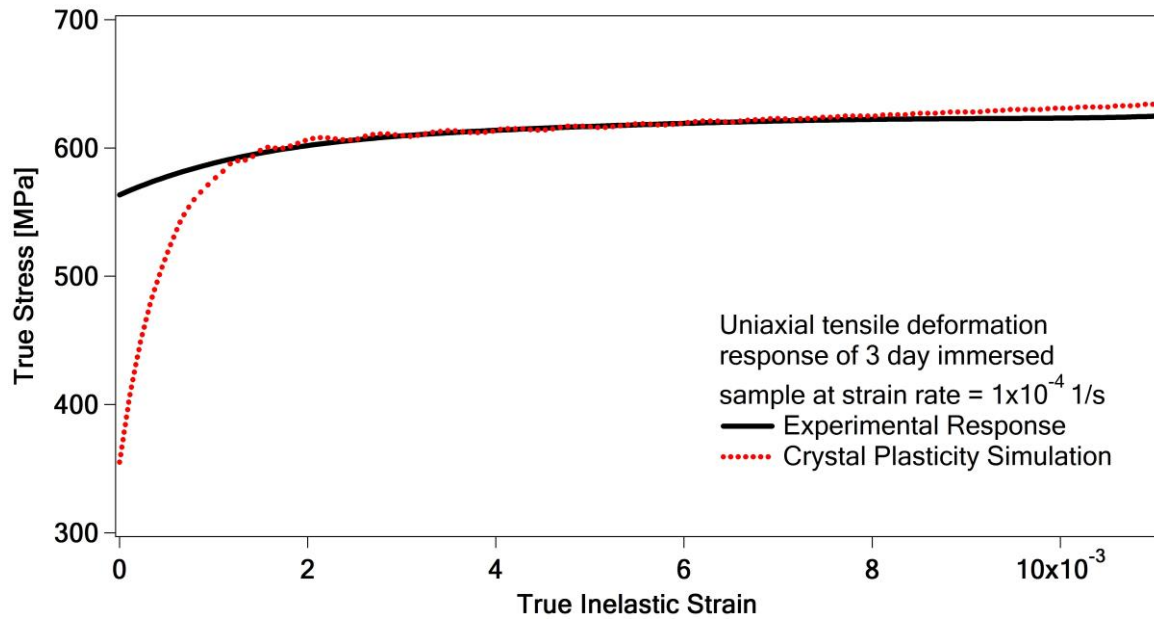


Figure 4. 15 Crystal plasticity simulation of the uniaxial tensile deformation response of the H-charged sample immersed for 3 days at a strain rate of 1×10^{-4} 1/s presented in comparison with the corresponding experimental result.

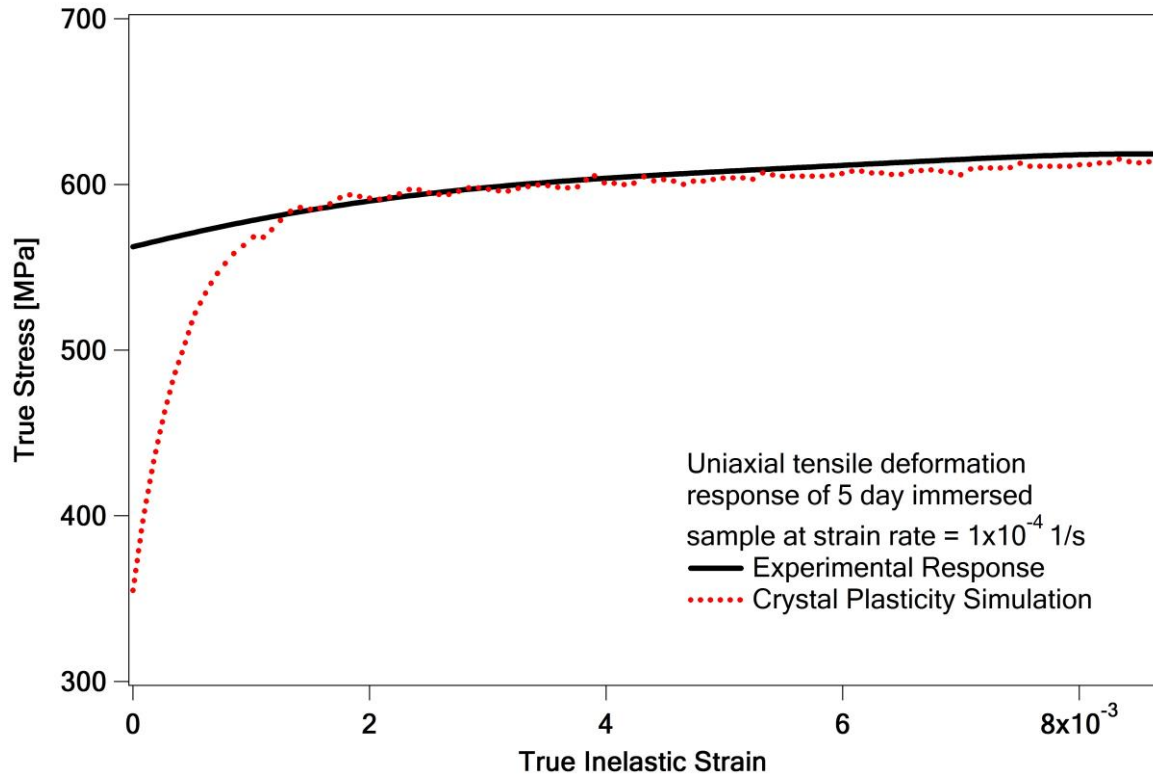


Figure 4. 16 Crystal plasticity simulation of the uniaxial tensile deformation response of the H-charged sample immersed for 5 days at a strain rate of 1×10^{-4} 1/s presented in comparison with the corresponding experimental result.

4.5 Conclusions

The current study was undertaken with the intention of improving the understanding of hydrogen embrittlement (HE). For this purpose, an iterative model was proposed to calculate the hydrogen (H) concentration around a single edge dislocation, which properly takes the relaxation effect into account. The model was then extended to compute the shear stress contribution of the time-dependent H concentration, which was incorporated into a visco-plastic self-consistent crystal plasticity model to predict the effects of H content on HE susceptibility. In order to verify our model, as-received and H-charged iron specimens were subjected to uniaxial tensile loading at moderate strain rates, and a comparison of experimental results with the corresponding simulation results revealed that the proposed

model is capable of calculating atomic level local instabilities imposed upon dislocation-H interactions and resulting macroscopic mechanical changes. H-induced softening and reduction in ductility, which is attributed to the HELP mechanism, were observed experimentally in the H-induced samples, and the experimental results overlapped well with the crystal plasticity simulations also on these aspects. Overall, the proposed model and the current findings shed light on the roles of H-interstitials and HE on the strain hardening behavior of rate-sensitive metallic materials.

4.6 References

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5 CHAPTER 5 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The motivation of the current work was to uncover the role of micro-deformation mechanisms on the performance of steels and alloys utilizing experimentation and multi-scale modeling effort. For this purpose, high strain rate tests were conducted to high-Mn alloys and corresponding microstructure examinations were carried out by optical microscopy, stereographic microscopy, scanning electron microscopy and transmission electron microscopy. Also, a unique multi scale modeling approach was proposed that incorporates the dynamic strain aging and hydrogen interstitials effects on the overall material response of studied materials into crystal plasticity.

First, the role of chemical composition and deformation temperature on the deformation response of two high-Mn steels were investigated with the aid of Charpy impact experiments (Chapter 2.2). Tests were conducted at three temperature in order to explore the temperature effect. Microstructural investigations prior to and after the experiments were performed by optical microscopy, scanning electron microscopy and transmission electron microscopy. Also, temperature change during the deformation was monitored with thermal camera. Overall, the results demonstrate that TWIP steel is deformed by two major twin systems at high temperatures, whereas, nano-twin formation within one primary twin system dominates at low temperatures. On the other hand, the deformation of XIP steel is dictated by slip at elevated temperatures and nano-twin formation within primary twins at low temperatures.

Next, three different types of high-manganese austenitic steels were subjected to high velocity compression load with the purpose of favoring twinning over slip (Chapter 2.3). In

order to investigate the role of temperature on the micro deformation mechanisms, three different testing temperatures were chosen to represent a wide temperature range: -170 °C to 200 °C and corresponding microstructure analyses were carried out. It was observed that formation of nano twins play crucial role on the strain hardening response of high manganese steels. Specifically, they were formed in Hadfield steel at all temperatures. For TWIP and XIP steels, on the other hand, they were prevalent at low and intermediate temperatures, respectively.

Following this analysis, in order to further investigate the deformation temperature and manganese content dependencies of microstructural activity in TWIP and XIP steels, high-velocity split-Hopkinson tensile experiments were conducted (Chapter 2.4). From transmission electron microscopy analyses, the ladder-like twinning activity was observed in TWIP steel at room temperature. Also, nano-twin formation within primary twins was observed in XIP steel at low temperatures. These two kinds of micro deformation mechanisms enhance the work hardening capacity of TWIP and XIP steels by providing additional barriers against dislocation motion.

This chapter of the study was followed by the incorporation the contributions of dynamic strain aging and the resulting negative strain rate sensitivity on the strain hardening response of Hadfield steel into crystal plasticity (Chapter 3). Specifically, the classical Voce type hardening model was modified by taking into account the flow stress contribution of interstitial carbon atom. Monotonic and strain rate jump experiments under uniaxial tensile loading were conducted at several strain rates in order to obtain the mechanical response of Hadfield steel. The simulation results demonstrated that the unique multi-scale modeling approach was both successfully predicts the mechanical response of Hadfield steel and the role of dynamic strain aging, and opens a new venue for accurately predicting the deformation response of rate-sensitive metallic materials.

Finally, after the successful analysis of dynamic strain aging modeling in crystal plasticity, hydrogen interstitial effect on the mechanical response of host matrix was experimentally investigated and numerically modeled (Chapter 4). Specifically, an iterative model was proposed to calculate the hydrogen (H) concentration around a single edge dislocation, which properly takes the relaxation effect into account. The model was then extended to compute the shear stress contribution of the time-dependent H concentration, which was incorporated into a visco-plastic self-consistent crystal plasticity model to predict the effects of H content on HE susceptibility. In order to verify authors' model, as-received and H-charged iron specimens were subjected to uniaxial tensile loading at moderate strain rates, and a comparison of experimental results with the corresponding simulation results revealed that the proposed model is capable of calculating atomic level local instabilities imposed upon dislocation-H interactions and resulting macroscopic mechanical changes. H-induced softening and reduction in ductility, which is attributed to the HELP mechanism, were observed experimentally in the H-induced samples, and the experimental results overlapped well with the crystal plasticity simulations also on these aspects. Overall, the proposed model and the current findings shed light on the roles of H-interstitials and HE on the strain hardening behavior of rate-sensitive metallic materials.

5.2 Future Work

The current findings in this study led to the further investigation of the deformation response of high-Mn steels under HE. For this purpose, a crystal plasticity model will be developed by incorporating DSA, slip-twin interactions and HE into the standard VPSC model. Specifically, a unique strain hardening model will be proposed that incorporates the atomic level local instabilities imposed upon by the pinning of dislocation by diffusing carbon

atoms, the interaction between the active slip systems and high density dislocation walls and shear stress imposed on arrested dislocations due to the surrounding hydrogen interstitials into the classical Voce hardening. The proposed work can be used in predicting the alterations in the performance of high-Mn steel based hydrogen storage materials, where hydrogen embrittlement is inevitable.

Furthermore, hydrogen concentration at the existence of both crack tip and an edge dislocation will be modeled. The corresponding stress field generated by diffused hydrogen atoms will be computed. The resulting changes in the micro-scale mechanical properties of the iron-based metallic matrix will be determined utilizing a VPSC approach. Finally, a finite element model that incorporates the outputs of both the atomic and microscopic level models will be employed to predict the crack propagation at the macroscopic scale. Despite the fact that the proposed work will focus on iron-based matrix, the outcomes will be applicable to all metallic storage materials to be utilized in hydrogen-fuelled applications.