Acta Materialia 142 (2018) 236–247

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Hydrogen embrittlement revealed via novel in situ fracture experiments using notched micro-cantilever specimens

Yun Deng**, Afrooz Barnoush*

Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

ARTICLE INFO

Article history:
Received 2 August 2017
Received in revised form
20 September 2017
Accepted 24 September 2017
Available online 26 September 2017

Keywords:
Hydrogen embrittlement
Micro-fracture mechanics
Transmission Kikuchi Diffraction (TKD) or transmission EBSD
FeAl intermetallics

ABSTRACT

The susceptibility of the FeAl intermetallic alloy to hydrogen-assisted cracking was investigated by in situ fracture experiments using notched micrometre-sized specimens using an Environmental Scanning Electron Microscope (ESEM). The notched beams were loaded under two different environmental conditions: one in high vacuum (5×10^{-4} Pa) to avoid hydrogen effects and one under a certain water vapor pressure (450 Pa) to promote hydrogen uptake. The fracture behaviour on a non-ASTM-standard micro-sized specimen was successfully studied by the experimental approach, and the microstructure of the whole crack area was analysed by Transmission Kikuchi Diffraction (TKD) and Transmission Electron Microscopy (TEM) techniques. Three crack growth stages were observed in all the specimens: i) elastic regime, ii) notch blunting and micro-crack formation; and iii) stable crack growth. We observed an accelerated crack propagation rate in specimens under hydrogen exposure. The hydrogen embrittlement phenomenon was found to occur because of the strong hydrogen-dislocation interactions. The combined effect of hydrogen-enhanced dislocation nucleation and hydrogen-restricted dislocation mobility is responsible for the hydrogen-enhanced cracking behaviour.

1. Introduction

Mechanical properties of metals and alloys are most often determined by interstitial atoms. Hydrogen (H), as one common interstitial element, is often found to degrade the fracture behaviour and lead to premature or catastrophic failure in a wide range of materials. Hydrogen embrittlement (HE) has thus been an important issue in hydrogen technology and has evoked intense scientific studies. However, with all the research efforts, HE is still one of the controversial questions and is particularly severe in iron-based alloys and steels because of the low solubility and high diffusibility of H in Fe [1]. For the metallic materials that do not form hydrides, the HE effects are always described commonly in one or a combination of the following models: 1) Hydrogen-enhanced decohesion (HEDE); 2) Adsorption-induced dislocation emission (AIDE); 3) Hydrogen-enhanced localized plasticity (HELP); and 4) Defactant mechanism.

The HEDE mechanism postulates that the hydrogen atoms attached to the crack tip reduce the cohesive bond energy between atoms and encourage a cleavage-like failure [2–6]. The mechanism received several controversies regarding the competition between the initiation of cracking and dislocation activity based on the experimental observations that large-scale plasticity can accompany slow crack growth in iron-silicon single crystals. However, the HEDE can still active when the dislocation emission is suppressed by the increasing dislocation blocking effects (pile-ups, dislocation locks) together with high H concentration driven by the very large triaxial stress near to the crack tip [7]. Moreover, the HEDE finds its huge popularity in explaining the intergranular fracture [8–11], which is rational since the strain constraint near the grain boundaries or phase boundaries requires multiple slip system activation, which produces opportunities for the cracking to occur through bond breaking. The AIDE states that hydrogen reduces the dislocation formation energy at the crack tip, thus promoting the crack propagation with dislocation emission from the crack tip at relatively lower stresses [12,13]. The above two models are obtained mainly from the posterior interpretation of the post-mortem morphological features obtained from macroscopic tests and lack some supporting evidence from direct experimental observations, or are supported mostly by simulations and models with several simplifications that remain to be validated. As an exception, the

* Corresponding author.
** Corresponding author.
E-mail addresses: yun.deng@ntnu.no, dengyun967514@gmail.com (Y. Deng), afrooz.barnoush@ntnu.no, afrooz.barnoush@gmail.com (A. Barnoush).

https://doi.org/10.1016/j.actamat.2017.09.057
1359-6454/

HELP is basically built on in situ observations of the dislocation motion in environmental transmission electron microscopy (ETEM) cells and states that the hydrogen atmosphere attached to the dislocation effectively shields the stress field in certain directions and thus allows the stress field to move in such directions at a lower stress level [14–21]. As a descriptive mechanism, the HELP has found widespread support since its first announcement. However, there are still disagreeing voices. The accelerated dislocation mobility in HELP via H reduced the degree of interaction of dislocations with other elastic singularities due to the H shielding effect [22], which is found not to be realistic in bcc metals since a large amount of H concertation (1.5×10^{-2} H/Me to reach the softening effect of 70 MPa) is required [23]. The experimental observation of "softening and hardening" as a common HE phenomenon in bcc iron was explained based on atomistic simulation with H-enhanced double-kink formation at high T or low H content, and H reduced kink-pair mobility at low T or high H content [24,25]. Song and Curtin [26,27] proposed that hydrogen reduces rather than enhances dislocation mobility based on atomic calculations. Recently, an opposite observation from an ETEM cell that dislocation will be locked by introducing H, and they argue that the locking effect is introduced by hydrogenated vacancy rather than atomic H [28], bringing about another hot but yet debated mechanism about hydrogen and strain-assisted vacancy production [29]. The defactant theory relies on statistical thermodynamics that predicts a reduction of defect formation energy to improve the generation rate, which has been observed directly from in situ TEM [30], and indirectly confirmed by in situ nanoindentation tests [31]. These mechanisms are hydrogen concentration, loading condition, and material dependence and are not necessarily mutually exclusive.

One of the major causes of the endless arguments of HE mechanisms roots in the difficulty of capturing the effect in the different time- and length-scales associated with the phenomenon. Hydrogen diffusion is considered fast and can vary from the test temperature and stress/strain state. The nontrivial H atoms-metal atoms, H atoms-defects and/or H atoms-crack interactions require an analysis under relevant atomic and/or the mesoscopic length scale either by computational modelling or by advanced experimental characterization. The existing experimental methods are either macroscopic tests providing only some phenomenal observations with low resolution, which lack revealing mechanistic understanding, or nanoscale tests inside ETEM offering chances to see direct H-defect interactions, which cannot ensure a certain constant strain/stress state or avoid the proximity effect from the sample surface with the tiny sample size used. Recent studies [32,33] of the micro-cantilever bending test with in situ hydrogen charging provide a good compromise by using the micro-sized sample that is small enough to sensitively capture the H effects while at the same time having enough volume capacity to avoid the shortages from ETEM tests. Another advantage of using a micro-sized sample is the possibility of the postmortem analyses of the overall sample rather than a selected part.

In this paper, the same experimental setup was employed with notched micro-sized cantilevers, and a simple case of H-induced cracking was investigated in detail, and a mechanism for crack initiation and propagation is proposed. The pure FeAl intermetallic single crystalline material was chosen as a model material to achieve a clean H-charging condition by the chemical reaction of Al with the water molecules (H_2O), provided by environmental scanning electron microscope (ESEM) as a default atmosphere, as well as to avoid the uncertainties caused by microstructural complications. More details can be viewed in previous papers [32,34].

2. Experimental details

2.1. Specimen preparation and testing techniques

The single crystalline FeAl was grown by a modified Bridgeman technique followed by an annealing process at 673 K for 120 h to eliminate the thermal vacancies [35]. From this specimen, cantilevers were milled by a focussed ion beam (Helios Nanolab Dual Beam FIB, FEI Inc., USA) to dimensions of ~3 × 3X12 μm using 93 pA at 30 kV as the final current to maintain a good surface quality. A lower current of 28 pA was used to introduce a sharp notch to each cantilever, 1.0 μm away from the cantilever beam support. The pre-notch was aligned to analyse the (001) [100] crack system, and the depth of the pre-notch was measured prior to testing from the side view. The notation of the crack system, (hkl) [uvw], gives the crystallographic plane (hkl) wherein the crack is located and the crack front direction [uvw]. The final geometry and test condition of all the beams are presented in Table 1.

After ex situ electron backscattered diffraction (EBSD) characterization, the beams were loaded in situ using the PI-85 Picoindent system (Hysitron Inc., USA) inside the ESEM (Quanta FEG 650 ESEM, FEI Inc., USA) under two different loading conditions: static loading and low cyclic loading. The static loading was applied with a 1.0 nm/s loading rate in the displacement-controlled mode. The dwell time between the loading and final unloading steps was 10 s. The low cyclic loading was applied by implementing partial unloading sequences after yielding with equal displacement interval of 200 nm. The loading and partial unloading speed were settled to be the same. Bending tests were performed under vacuum (~5×10^{-4} Pa), i.e., hydrogen free, and water vapor ESEM (450 Pa, 900 Pa) conditions, i.e., hydrogen charged.

2.2. t-EBSD and TEM characterization

To visualize plastic deformation with relatively high resolution, a novel transmission EBSD (t-EBSD) was performed on the cracking area after tests. The major difference between t-EBSD and normal EBSD is that the sample used is electron-transparent and mounted horizontally or back-tilted away from the EBSD detector. With this

Table 1
Beam dimensions (in μm), test conditions and test methods. The symbols L, B, w, a, represent the length, width, thickness, and initial notch depth of the beam shown in Fig. 1.

Beam No.	L	B	w	a	Test Conditions	Final Depth	Test Methods
V1	11.34	2.97	3.212	689.0	Vacuum	3.5	Static loading
V2	11.31	2.84	3.193	593.6			
E1	11.50	2.91	3.135	632.7	ESEM (450 Pa)		
E2	11.41	3.06	3.168	649.4			
E3	11.47	2.88	3.135	580.6	ESEM (900 Pa)	2.0	
V3	11.02	3.25	3.00	383.1	Vacuum	4.5	Cyclic loading
V4	11.03	3.209	3.01	410			
E3	11.05	3.031	3.016	395.0	ESEM (450 Pa)		
E4	11.05	3.157	3.094	392.9			