Materials Science & Engineering A 577 (2013) 105–113

Contents lists available at SciVerse ScienceDirect

Materials Science & Engineering A

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

Special fracture behavior of nanocrystalline metals driven by hydrogen

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ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form
2 April 2013
Accepted 7 April 2013
Available online 11 April 2013

Keywords:
Nanocrystalline metals
Hydrogen embrittlement
Brittle fracture
Dislocation emission
Dislocation free zone

ABSTRACT

The embrittlement of conventional metallic systems by hydrogen is a well documented phenomenon. However, the precise role of hydrogen in this process for nanocrystalline materials is poorly informed and comprehensive theoretical models are not available yet. Here, a new model is proposed wherein hydrogen atoms accumulate before a nanocrack tip and interact with piled up dislocations ahead of dislocation free zone (DFZ) actively. The interaction between hydrogen atoms and dislocations can prevent dislocations emitting from nanocrack tip, and thus suppressing nanocrack tip blunting and ductile fracture while promoting brittle failure. In addition, the size of DFZ in nanograins was analyzed from the macro–micro fracture mechanics point of view and the relative computing method was derived. The dependence of maximum number of dislocations emitted from nanocrack tip on grain size with and without hydrogen in nanocrystalline Ni is clarified and compared. The results show that the introduction of hydrogen into nanocrystalline materials gives rise to a reduction in critical crack intensity factor more than 30% in contrast with hydrogen free case, and this special fracture behavior driven by hydrogen atoms is especially remarkable with the reduction of grain size.

1. Introduction

The embrittlement of metallic systems by hydrogen is a kind of serious environmental failure that affects almost all metals and their alloys. With the development of technology and the establishment of low-carbon society, the usage of high-strength structural materials for lightweight construction and energy conservation becomes a necessity. Although material scientists try their best in developing alloys that integrate excellent tensile strength with prominent fracture toughness, hydrogen embrittlement still poses a widespread hazard to the fracture resistance of metallic materials. Moreover, with the depletion of fossil fuels, mankind is searching for additional alternative energy. Hydrogen is believed to be an appropriate substitute energy source and it is most likely that a "hydrogen-based economy" will be realized within the next several decades. In this particular case, large-scale production, storage, transportation and utilization of hydrogen will become inevitable. However, detrimental problems that accompany the employment of hydrogen are substantial. Of vital significance is the impairing effect of hydrogen on the mechanical properties of materials, particularly high strength steels and nickel, where hydrogen uptake in the metal can induce premature, unexpected and potentially catastrophic failures [1]. The degradation in mechanical properties of metals due to hydrogen is often followed by a sharp transition in fracture mode from ductile fracture (i.e. strain controlled microvoid coalescence) to brittle fracture (i.e. stress controlled intergranular cracks propagation) [2–8], despite substantial plastic deformation may still occur in this embrittling process. For example, slip trace along the fracture path is observed in high-resolution fractography when embrittlement occurs in Ni and its alloys [3–5,9–12].

Ever since 1874, scores of scientific predecessors devote themselves to filling in this blank field. Although extensive experimental and theoretical studies have brought about various mechanisms concerning hydrogen-induced embrittlement, the conclusive predictions for hydrogen embrittlement that reflect the fundamental mechanisms have remained unavailable. One feasible reason that accounts for this embarrassment may be that each candidate is supported by its specific experimental observations, theoretical hypothesis and personal views. Among the diversified proposals, three candidates seem to be quite fascinating, namely (i) hydrogen-enhanced decohesion (HEDE) [13–18], where the segregation of hydrogen atoms at internal interfaces is assumed to weaken the surface cohesive energy there, and facilitate more cleavage-like brittle failures consequently. This theoretical model was based upon several experimental observations [18–20]. (ii) Hydrogen-enhanced local plasticity (HELP) [21–22]. In the HELP mechanism, hydrogen atom is expected to decrease the motion barriers for dislocations, thereby aggravating the extent of plastic deformation that occurs

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http://dx.doi.org/10.1016/j.msea.2013.04.019

in a relatively localized region adjacent to the fracture surface [23]. The fracture process is not so much a hydrogen-induced brittle failure as a highly localized plastic deformation. (iii) Hydride formation and cleavage [24–26]. This suggestion is viable under the specific circumstances where hydride is feasible to form, and this "new comer" is thought to provide a "low energy" fracture path for brittle failure [27].

Generally speaking, while each proposal has its unique merits, and while different proposals may be suitable for different materials, none of them have a solid proof to explain the existing phenomenon concerning hydrogen embrittlement for nanocrystalline materials comprehensively. Hence, more in-depth experimental and theoretical investigations are welcomed in this field.

Here we propose a mechanism for hydrogen embrittlement in which we focus on the sharp transition from ductile fracture to brittle one. Particularly, our efforts are devoted to quantifying the aggravated effect of grain size on maximum number of dislocations emitted from a nanocrack tip under the circumstance where hydrogen atmosphere is formed in nanocrystalline materials. The distinguishing feature of this work is that by employing the present model, one can clarify the size dependent relationship between grain size and dislocation free zone (DFZ). In the framework of our theoretical model, it is assumed that hydrogen atoms accumulation around the rim of DFZ prevents dislocations emission from the nanocrack tip, and thus suppresses crack-tip blunting while impelling brittle failure. At the same time, whether the nanocrack propagates or not is considered to be of vital significance in the failure course of nanocrystalline materials. A detailed process can be seen in Fig. 1. Fig. 1(a) shows that a nanocrack becomes blunt due to dislocations emission without the invasion of hydrogen atoms. On the contrary, with the introduction of hydrogen atoms, a rather distinctive event will occur. As can be seen in Fig. 1(b), substantial hydrogen atoms accumulate against DFZ which just lie in the immediate front of the nanocrack. The existence of hydrogen atoms suppresses further dislocations emission and prevents nanocrack from blunting. Consequently, it advances forward dramatically.

The remainder of this paper is aimed at verifying the mechanism sketched above by means of micro-mechanics and numerical analysis in Ni–H system, and it is structured as follows: In Section 2.1, the stress field of DFZ around the pre-existing nanocrack in nanocrystalline materials was described. In Section 2.2, the classic Von Mises yield criterion and the Hall–Petch relationship were employed to predict the size dependence of DFZ upon grain size for a pre-cracked nanocrystalline bulk. In Section 2.3, the comprehensive effect of grain size and hydrogen atoms on dislocation nucleation and brittle fracture in Ni–H system at room temperature was studied. In Section 3, the developed model was discussed further on the basis of the results that we obtained. In Section 4, within the theoretical frame of this work, a more conclusive idea about the mechanism that we recommended is summarized.

2. Hydrogen-induced aggravated effects of grain size on crack blunting in nanocrystalline materials

2.1. The stress field around DFZ in nanocrystalline materials

Both experiments and previous theoretical analyses [28–33] imply that brittle-cleavage process is driven by dislocation piled up against the DFZ, and a trigger point mainly locates at the tip of piled-up dislocations that are adjacent to a nanocrack tip. Consequently, the size of DFZ is of vital scientific importance in understanding the brittle versus ductile behavior caused by hydrogen in nanocrystalline materials.

The formation of DFZ in nanocrystalline materials means that a square-root stress singularity in the immediate vicinity of the nanocrack tip is restored, and it is feasible to characterize the highly distorted and localized stress field near/at the nanocrack tip

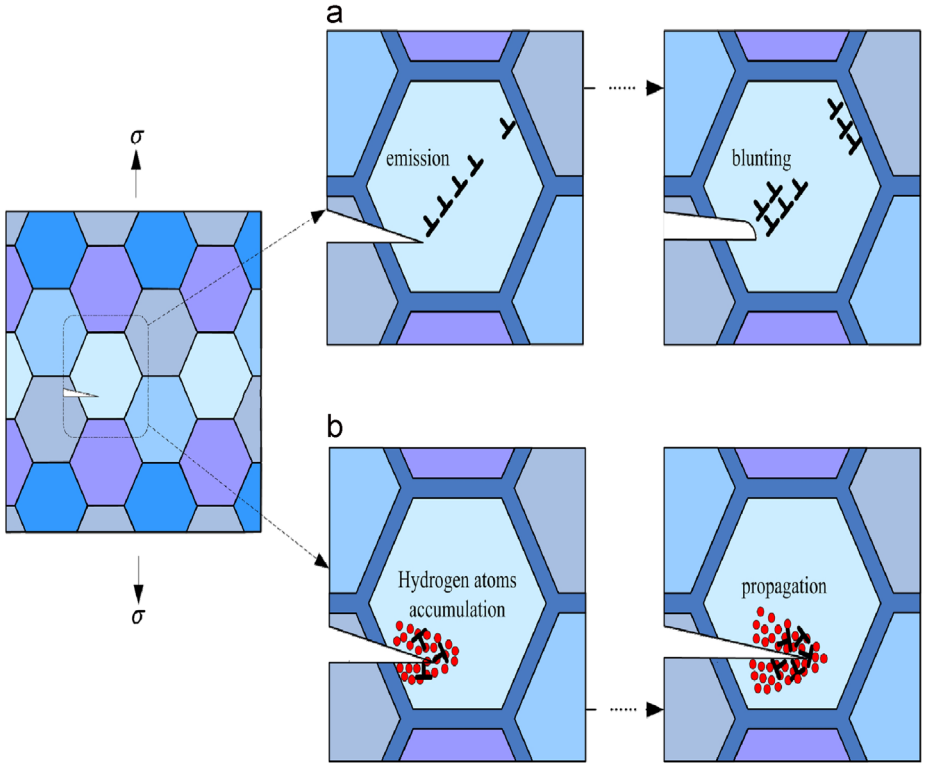

Fig. 1. A schematic of the evolution of a pre-existing nanocrack which is subjected to a remote loading: (a) without the attendance of hydrogen atoms, the nanocrack is blunted by emission of dislocations from the crack tip, and (b) with the introduction of hydrogen atoms, they segregate near the nanocrack tip substantially and inhibit dislocation emission, favoring brittle fracture in return.