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Direct evaluation of grain boundary hydrogen embrittlement: A micro-mechanical approach

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ABSTRACT

In order to directly investigate the grain boundary (GB) hydrogen embrittlement in polycrystalline materials, a novel micro-mechanical testing method was developed. By combining a site-specific sampling technique and a high-voltage environmental transmission electron microscope (HV ETEM), the fracture property of micro-cantilever specimens fabricated from the *same* GB in a nickel-aluminide (Ni_3Al) polycrystal was critically compared in environments with/without hydrogen (H_2) gas. For randomly oriented GBs, brittle fracture nucleation accompanied by plastic deformation was observed in a H_2-containing environment except for ones with small orientation difference. No GB fracture was observed for coherent $\Sigma 3$ boundaries. It also appeared that the similitude of the hydrogen-enhanced decohesion (HEDE) mechanism was still valid even for the submicron-scale specimens.

1. Introduction

The mechanical strength of crystalline materials is strongly influenced by grain boundaries (GBs) where differently oriented crystals are bound. In an environment where hydrogen is either contained or supplied by a chemical reaction, subcritical crack growth is found to occur particularly in high-strength metals subjected to a sustained (or incremental) load [1,2]. Such a phenomenon, one manifestation of the so-called hydrogen embrittlement (HE), is frequently accompanied by intergranular fracture and/or quasi-brittle transgranular fracture [1–5]. As to the hydrogen-induced GB fracture, which is the subject of this study, the phenomenon has been observed not only in high-strength engineering alloys but also in low-strength pure metals (e.g. Ni [6–8]) where segregation of other impurity elements to GBs was completely absent.

The mechanism of hydrogen-induced GB fracture has been studied for decades. The most fundamental aspect of the issue is the effect of hydrogen on the cohesive energy of GBs. As no experiments are effectual for revealing this point, it has been specifically addressed by atomic simulation [9–11]. Although the results are still limited to simple systems, they have successfully indicated the reduction of cohesive energy. It is, however, rather jumping to explain the actual GB fracture with this intrinsic decohesion alone. One has to admit that plasticity (dislocation activity) generally attends fracture in metals, and the near-GB hydrogen concentration may be affected by plasticity in the case of HE problem [12]. The susceptibility to HE seems to be also dependent on GB characteristics (orientation difference and/or coherency) as envisaged by the fractography showing mixture of GB/transgranular fracture [3,8,13]. This is probably attributed to the difference in the collaborative effect of both intrinsic decohesion and other extrinsic factors which is specific to each GB. The conventional experiments using bulk polycrystalline materials, however, only provides statistical tendency of GB fracture as a function e.g. of macroscopically averaged hydrogen concentration. The mechanism of hydrogen-induced GB fracture will then be effectively investigated if the strength of a *discrete (unit)* GB in polycrystalline materials is directly evaluated.

In the last decade, the advancement of micro-mechanical tools, combined with micro-fabrication techniques, has enabled researchers to directly probe the mechanical response of a discrete GB in a polycrystal [14–17]. Such a method has been applied e.g. to the detection of stress corrosion cracking (SCC) in SUS304 [14], the measurement of the fracture toughness of bismuth (Bi)-embrittled copper (Cu) GBs [15], the strength evaluation of pre-oxidized GBs in nickel-based Alloy 600 [16] or GBs in a high strength aluminum alloy (A2198) [17]. These examples, all of which were done by the normal nanoindenter-based technique, are notable as they

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substantiated, in part, the feasibility of the long-desired experiments. They also have essential advantages over the conventional tests using large bicrystal specimens that artificially simulate minute GBs. From the viewpoint of HE, however, similar experiments have not been reported. This is partly due to the difficulty associated with the precise control of hydrogen environment. Besides, the effect of hydrogen on GB fracture should be ultimately discussed with the comparative data obtained from the *same* GB, but such an ideal experiment is still, in reality, difficult to be achieved by the normal nanoindenter technique.

The aim of this study is firstly to develop a novel approach that enables the mechanical testing of a GB under controlled gaseous environments. The effect of hydrogen gas on the fracture property of GBs is then discussed on the bases of comparative data obtained from the *same* GB. Such a challenging task, to the best of our knowledge, has never been reported to date.

2. Materials and methods

The material used in this study was a wafer of high-purity (> 99.9%) polycrystalline Ni_3Al (Ni:Al = 0.75:0.25) having average grain size of 110 μm. This material has ordered face-centered cubic (FCC) structure at room temperature. The crystallographic orientation of electropolished surface was firstly analyzed by electron backscattered diffraction (EBSD) method. Then, relatively long GBs (length: ≈ 100 μm) with straight profile were selected so as to duplicate a couple of specimens from the same GB.

Fig. 1 schematically shows the specimen fabrication procedure. The specimen was fabricated by a site-specific micro-sampling technique: a block containing the target GB was cut out by focused ion beam (FIB) and transferred to an open stage (in this study, a metal wire) for forming a cantilever shape [18]. Note that a special care was taken so that the final GB plane was placed normal to the neutral axis of the cantilever. A wedge-shaped notch (opening angle:90°) whose corner was placed at the GB was introduced. The additional carbon layer attached to the lever end serves as a hard contact pad that effectively avoids indent formation during loading. Fig. 2 shows an example of a secondary electron (SE) image of a specimen. The thickness of specimens was ca. 350–620 nm. The GBs used for comparative tests are listed in Table 1.

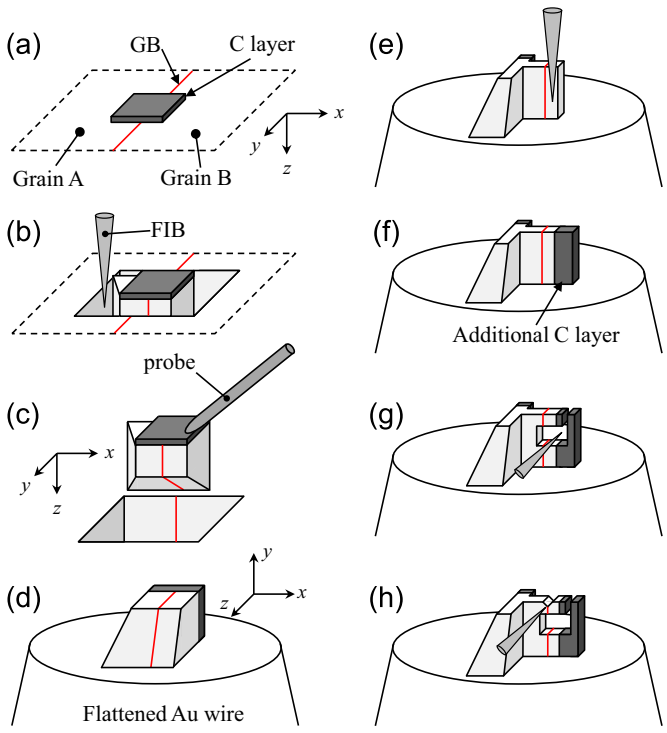

Fig. 1. Fabrication procedure of a micro-cantilever specimen containing a discrete grain boundary (GB): (a) carbon layer deposition; (b) trenching; (c) pick up; (d) stage mounting; (e) thinning; (f) additional carbon layer deposition; (g) cantilever formation; (h) notch introduction at GB.

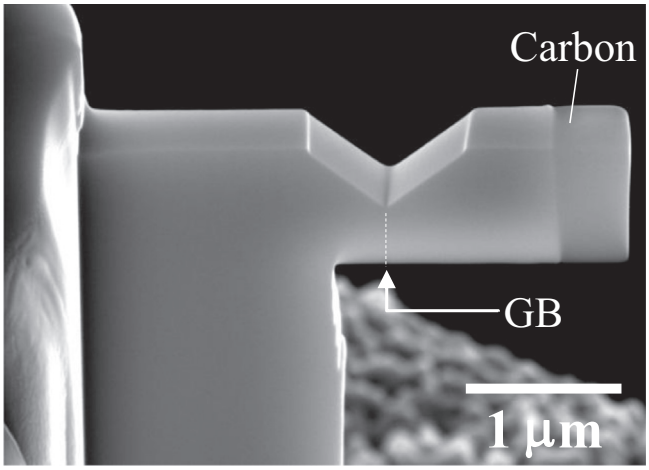

Fig. 2. A micro-cantilever specimen containing a discrete GB at a V-notch tip.

The experiments were conducted inside the Reaction-Science High-voltage Electron Microscope (RSHVEM) at Nagoya University (JEM-1000K RS, JEOL). It is equipped with an environmental cell (EC) that is either inserted to or retracted from the column *on demand* [18,19]. The EC, which is aperture-limited type, can be combined with various types of sample holders. In this study, a single-tilt nanoindenter holder (HN200E, Nanofactory) was used. The cantilever specimen was approached to a diamond indenter tip, and their relative position was precisely controlled by piezo fine movement. The specimen was loaded by moving the sample stage in a stepwise manner (1 nm per 2 s). The applied load was measured with a micro-load sensor located behind the indenter tip. The tests were conducted either in vacuum or N_2-20 vol%H_2 gas (hydrogen partial pressure: $p_{H2} = 1$ kPa). A high acceleration voltage of 1000 keV was employed to facilitate the dissociation and ionization of gas molecules [20,21] as well as to avoid the image degradation by gas-induced electron scattering.

3. Results

Fig. 3 shows the results of experiments conducted in vacuum: load-displacement (P-δ) curves and micrographs of a specimen (GB No. 4, orientation difference:40.6°). Here, the abscissa of Fig. 3 (a) indicates stage displacement, and it can be regarded as specimen deflection as the rigidity of other parts is far larger. After an initial linear deflection regime, slight amount of work hardening follows. Then, significant amount of plasticity continues with little hardening. The initial hardening is attributed to dislocation pile-up around the GB and cantilever root where dislocation activity was most prominent. The subsequent plasticity under constant load is caused by swept-out dislocations activated at the other part of the specimen. The loading was continued until the contact point between the indenter and specimen severely shifted from the initial position due to extreme bending. In the case of GB No. 4, the loading ended in gradual load reduction accompanied by necking and cracking at the notch-tip region. Post-experimental observations confirm a ductile GB fracture with out-of-plane slip separation (see Fig. 3(c) and (d)). It should be noted that all the other GB samples, except for No. 8 that showed similar fracture behavior as