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On the study of the oriented cracks formed in ErD_2 thin film

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ABSTRACT

Pure erbium (Er) film was grown on molybdenum substrate by an electron-beam evaporation deposition technique. Cracks along the {111} crystal planes of ErD_2 lattice have been found to grow in ErD_2 films synthesized by deuteration of metal Er films. The preferentially orientated cracks consist of polycrystalline Er_2O_3 particles, which are well confirmed by chemical analysis via X-ray energy dispersive spectroscopy (EDS) element mapping and selected area electron diffraction (SAED) performed in a transmission electron microscope (TEM). Two main factors are thought to account for the formation of the orientated cracks. One is the increase in local stresses caused by the phase transformation from Er to ErD_2, the other is the oxygen diffusion to the favored sites in ErD_2 lattice during deuteration processing.

1. Introduction

Formation of metal hydrides via interaction of hydrogen (H) with metals is an effective approach for hydrogen storage [1]. These metal hydrides have attracted much attention in recent years due to their potential applications in many industry fields, for example, as fuel cells [2,3], thermocompressors [4] and actuators [5]. However, cracks have been reported to form during hydrogenation. These can be detrimental to the mechanical properties of the metal hydrides, limiting their practical applications [6]. Hydrogen-induced embrittlement has thus been an important issue to be resolved. Much research has been conducted on the fracture initiators [6–9]. Dutton et al. [7] reported that the tensile stress induced by the hydrogenation increases the H migration towards the crack tips. In a recent publication, Song et al. [8] proposed a ductile-to-brittle transition mechanism caused by the suppression of dislocation emission at the crack tip due to aggregation of H. Erbium tritide (ErT_2) film is under consideration as a candidate target material for a neutron generator, due to its high thermostability [10,11]. Processing effects on the microstructure in Er and ErD_2 thin films have been conducted by Parish et al. [10], who did not observe deuteration induced cracks in the ErD_2 film. Rodriguez et al. [12] found that the preferential helium (He) bubbles form in ErT_2 film, and macrostrain due to He bubble growth is empirically detected by a $\sin^2 \Psi$ method. The He bubbles would act as barriers to the dislocation movement and harden the material, thus causing the degradation of mechanical property of ErT_2 film [13,14].

In the present study, we observed the formation of intragranular cracks in the Erbium deuteride (ErD_2) films, and the cracks preferentially grow along the specific direction in the ErD_2 lattice. The generation of the orientated cracks is thought to be due to not only the increased local stresses induced by the deuteration process but also the oxygen diffusion to the crack tips.

2. Experimental procedure

Pure Er thin film on molybdenum was prepared by electron beam deposition at a substrate temperature of 350 °C and a deposition rate of 10 nm/s with the chamber vacuum better than 3.0×10^{-6} Torr. The Er film was then transferred to a home-made metal hydrogenation apparatus for erbium deuteration immediately. To obtain erbium deuteride (ErD_2) thin film, the pure Er film was firstly heated to 600 °C in a vacuum chamber with a base pressure of ~3.0×10^{-6} Torr, where amount of pure D_2 gas was then flowed in to deuterate the Er film. The D_2 gas was produced by heating a uranium bed where the D_2 gas was stored as uranium deuteride. The pressure of D_2 gas in the chamber is measured by a diaphragm gage as ~20 Torr while deuteration. After the Er film had been exposed to D_2 gas atmosphere for up to 30 min, the D_2 was outgassed from the chamber allowing the sample to be cooled naturally to room temperature. Cross-sectional view specimens for transmission electron microscopy (TEM) study were prepared using an in-situ focus ion beam (FIB) lift-out method performed in a FEI-Helios 650 FIB instrument. TEM and Scanning TEM (STEM)

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characterizations, including bright-field (BF), dark-field (DF), annular dark-field (ADF) and high-resolution electron microscopy (HREM) imaging and selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) were performed on a JEOL 2010F TEM working at 200 kV.

3. Results and discussion

Fig. 1(a) and (c) shows BF images of the cross-sectional view of ErD_2 thin film. Preferentially oriented cracks are visible in the ErD_2 film. The SAED patterns are shown in Fig. 1(b) and (d), which are taken from the A1 and A2 areas circled in Fig. 1(a) and (c). Fig. 1(b) shows only one set of diffraction pattern because it was taken from a single fcc-ErD_2 grain along its [011] direction. Analysis of the SAED pattern suggests that the cracks in the corresponding BF image grow along the {111} crystal planes of the ErD_2 lattice. There are more features in the SAED pattern shown in Fig. 1(d). Besides two sets of strong diffractions, a set of ring pattern can also be observed. The two sets of strong diffractions are from two pieces of single grain ErD_2 phase twining along their {111} planes. The polycrystalline rings are indexed as the (211), (222), (332) and (440) crystal planes of the Er_2O_3 lattice. It indicates that many Er_2O_3 particles have been formed in the film with the cracks.

A magnified BF image of a crack is shown in Fig. 2(a) with an inset showing HREM image of the crack. A DF image on the basis of the Er_2O_3 polycrystalline rings is also shown in Fig. 2(b), in which bright contrast features of Er_2O_3 particles distribute in the whole ErD_2 film, especially on the edges of cracks. It demonstrates that the orientated cracks are composed of many Er_2O_3 nanoparticles, instead of a real gap.

The EDS element maps of O and Er are shown in Fig. 3. Fig. 3(a) shows an ADF image, whose intensity is sensitive to variations in the atomic number of atoms in sample or the thickness of the sample. From the image we can see that the intensity of the image in the cracks is lower than that of the crack-free areas. This suggests that these crack regions either have more light elements or have no materials at all. In order to further identify the nature of these cracks, O and Er element profiles along Line 1 shown in Fig. 3(a) are plotted in Fig. 3(b). Four peaks, labeled as a, b, c and d, are observed in the line spectrum of O element. The locations of the four peaks are consistent with that of cracks, indicating the preferential formation of the Er oxides in the cracks. Fig. 3(c) and (d) depicts O and Er element maps which shows that the Er_2O_3 particles are dispersed in the whole ErD_2 film and mainly in the oriented cracks.

To understand the growth mechanism of the oriented cracks in the ErD_2 film, it should be addressed that the phase transformation from Er to ErD_2 would be accompanied by the lattice expansion from 0.061 nm^{-3} for hcp-Er to 0.134 nm^{-3} for fcc-ErD_2 during deuterium loading. The macrostresses would be induced by the lattice expansion that is reported by Allain et al. [15], who measured the lattice strain during in-situ gas phase deuterium loading of Nb films on sapphire with X-ray diffraction. The mechanism of phase transformation from metal to metal hydride for titanium (Ti) has been well established in terms of atom diffusion and lattice rearrangement [16]. Xiao [16] describes the transformation of an hcp structure for Ti into an fcc structure for Ti hydride as the passage of $1/3<100>$ shearing. The shearing process is driven by the reduction in Gibbs free energy of the system due to the hydride formation. The lattice misfits are visible at the interface of metal and metal hydride in the HRTEM for the specific case of Ti by Bourret et al. [17] and Xiao [16]. The build-up of crack tip involves the diffusion of hydrogen along the stress field that is caused by the lattice misfit [6]. The {111} crystal planes are the major slip system for the metal hydride with fcc crystal structure, as those planes have largest lattice distances. As for ErT_2 film, in which He atoms decaying from T would aggregate to form He bubbles with preferential orientation along {111} planes [12]. The macro-strain is induced by the formation of He bubbles

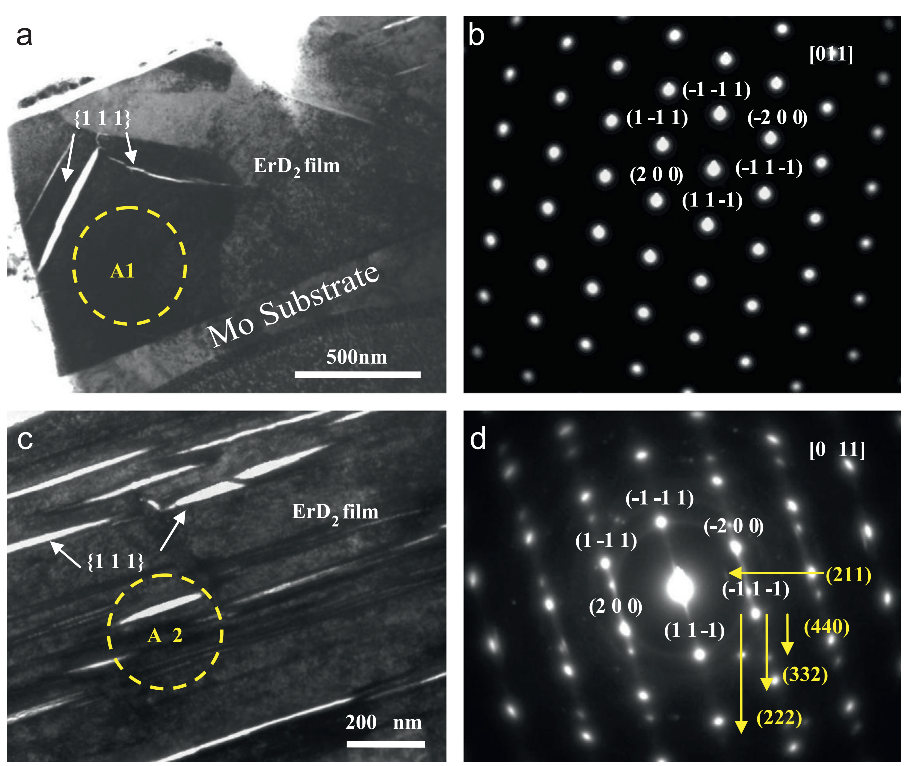

Fig. 1. The cross-section BF images ((a) and (c)) and corresponding SAED patterns ((b) and (d)) of molybdenum supported ErD_2 film. It is clear that some oriented cracks appear in the ErD_2 film from (a) and (c). The indexed SAED patterns (b) and (d), stemming from the A1 area in (a) and A2 area in (c) with the zone axis of [011], confirm that all the cracks grow along the {111} crystal planes of ErD_2. There appears some diffraction rings in (d), where the positions are in agreement with the diffractions of Er_2O_3.