***In Situ* TEM Observations of Liquid Metal Embrittlement of Al Single Crystals in Hg + 3 atm% Ga**

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Keywords: Aluminium Single Crystal, TEM, Liquid Metal Embrittlement

ABSTRACT

The change in dislocation configuration ahead of a loaded crack tip, before and after adsorbing Hg atoms, and the initiation of liquid-metal-induced nanocrack (LMIC) have been *in-situ* observed using a special TEM constant-deflection device. The results show that chemisorption of Hg atoms facilitates dislocation emission, multiplication and motion. A LMIC is initiated either in the dislocation free zone (DFZ) or at the crack tip when the chemisorption-facilitated local plasticity is developed to a critical level. A new mechanism of liquid metal embrittlement (LME) is accordingly proposed that chemisorption of Hg atoms reduces the surface energy, leading to reduction in both the critical stress intensity factor for dislocation emission and the resistance to dislocation motion. Consequently, the plastic work, γ_p , and the fracture toughness, K_{IC} , are decreased and the samples fracture in a brittle mode.

1. INTRODUCTION

Fractograph of LME failures revealed localized plastic deformation (LPD), and thus Lynch proposed the model of chemisorption-enhanced LPD [1]. However, direct observations of chemisorption-facilitated dislocation emission, multiplication and motion have not been conducted yet, and the relationship between the chemisorption-enhanced LPD and the initiation of LMICs is still unclear so far. Therefore, they are the tasks of the present work. In order to implement *in situ* TEM observations, we design and manufacture a special constant-deflection-loading device [2]. With this device we study the effects of chemisorption on dislocation emission and motion by observing changes in dislocation configuration ahead of a loaded crack tip before and after chemisorption of liquid metal atoms.

2. EXPERIMENTAL PROCEDURES

The material used in this study was Al single crystals. A strip of 0.2 mm thickness was cut and thinned to about 0.1 mm by means of mechanical polishing. The foil specimens for *in-situ* testing were prepared by jet polishing with an electrolyte of 26% HNO₃ + 74% CH₃OH. The specimen surfaces were finally cleaned by ion bombardment.

The foil specimen was installed on the device and loaded by a screw to generate a slit crack in the thinned region [2]. Then, the loaded specimen was aged at room temperature under the constant deflection for 20~24 hrs until the dislocation configuration around the crack tip is stabilized, which was checked by taking two TEM pictures at a time interval of one hour. In this way, we avoid the creep influence on the dislocation emission and motion during LME. After that, the device with the foil was put above the liquid metal of Hg + 3 atm% Ga [3] for a period of time, and then examined again by TEM. All TEM observations were carried out in a H-800 microscope.

3. RESULTS

3.1. Chemisorption-Facilitated Dislocation Emission and Motion

The stable dislocation configuration in front of a loaded crack tip of sample 3 precrept in air at 50 °C for 20 hrs is shown in Fig. 1a, where "A" denotes the crack tip. As can be seen in Fig. 1a, there are few dislocations ahead of the loaded crack tip. After exposing the sample above the liquid metal (Hg + 3 atm% Ga) at 50 °C for 40 min., however, a group of inversely piled-up dislocations was generated in front of the crack tip, as shown in Fig. 1b. Since the group of dislocations "BC" is piled up near the crack tip, they must be emitted from the crack tip. This indicates that chemisorption of the liquid metal atoms facilitates dislocation emission from the loaded crack tip.

Fig. 1. Chemisorption-facilitated dislocation emission: (a) pre-creeping at 50 °C for 20 hrs and (b) exposing to atmosphere of Hg + 3 atm% Ga at 50 °C for 40 min.

Fig. 2. Chemisorption-facilitated dislocation emission and motion: (a) pre-creeping at 50 °C for 20 hrs, (b) exposing to atmosphere of Hg + 3 atm% Ga at 50 °C for 40 min, and (c) further exposing for another 20 min.

Fig. 2a shows the dislocation configuration ahead of the loaded crack tip of specimen 2 precrept in air for 20 hrs and in TEM for about 0.5 h. There are many dislocations in the region of "HG". After putting the device with the foil above the liquid metal at 50 °C for 40 min, however, the dislocations in "HG" moved away from the visual field and a group of new dislocations "BC" piled up near the crack tip, as shown in Fig. 2b. After putting it again above the liquid metal at 50 °C for another 20 min., the dislocations at the position of "BC" shown in Fig. 2b disappeared and a row of new dislocations "DE" emerged on the top of the crack, as shown in Fig. 2c. Since the dislocation row "DE" is on the top of the crack and behind the crack tip, it is obvious that the group of dislocations "DE" must be generated from a dislocation source near, rather than emitted from, the crack tip. Therefore, dislocation emission, multiplication and motion occurred during LME under a stress intensity factor lower than the critical value for dislocation emission and motion in the absence of a liquid metal environment. That is to say that chemisorption of liquid metal atoms facilitates the dislocation emission, multiplication and motion.

It should be noted that the crystal direction remained unchanged before and after the constant-deflected specimen was placed above the liquid metal, and the dislocation configuration ahead of a loaded crack tip reached a steady state after maintaining a constant deflection for more than 20 hrs. Thus, the change in the dislocation configuration induced by putting the specimen above Hg +3 atm% Ga for some time period must be produced by chemisorption of the liquid metal, rather than from changes in diffraction condition and thermal activity.

3.2. Initiation of LMIC in DFZ or at the Crack Tip

Fig. 3a illustrates the dislocation configuration of specimen 4 pre-crept at 50°C in air for 20 hrs, where "BCD" marks DFZ. After exposing the specimen in the atmosphere of Hg + 3 atm% Ga at 50 °C for 40 min, the dislocation configuration was changed, as shown in Fig. 3b. The DFZ is enlarged into "BED" and the dislocations in the region of "DEF" shown in Fig. 3a were removed from the visual field, but the crack tip did not propagate. Fig. 3c shows that a microcrack "e" initiated at the crack tip after further exposing in the atmosphere of Hg + 3 atm% Ga for 7hrs. The results show that the LMIC was initiated only when chemisorption-enhanced dislocation emission and motion developed into a critical level.

Fig. 3. The continuous initiation and propagation of a LMIC: (a) pre-creeping for 20 hrs in air at 50 °C, (b) exposing in atmosphere of Hg +3atm% Ga at 50 °C for 40 min, and (c) exposing in atmosphere of Hg + 3 atm% Ga at 50 °C for 7 hrs.

Fig. 4. The discontinuous initiation and propagation of a LMIC: (a) pre-creeping for 20 hrs in air at 50 °C, (b) exposing in atmosphere of Hg + 3atm% Ga at 50 °C for 5 hrs, and (c) exposing in atmosphere of Hg + 3 atm% Ga at 50 °C for 5 hrs.

Fig. (4) is an example of discontinuous initiation of a LMIC in specimen 5 which was precept for 20hrs in air. After placing the specimen above the liquid metal for 5 hrs, a microcrack "e" was discontinuously nucleated in the DFZ, while the main crack opened by emitting dislocations, as shown in Fig. 4b. Exposing the specimen again into the atmosphere of Hg + 3 atm% Ga for 5 hrs resulted in connection of the microcrack "e" to the main crack, as shows in Fig. 4c.

4. DISCUSSION

4.1. Chemisorption-Facilitated Dislocation Emission and Motion

The critical stress intensity factor K_{Ic} for dislocation emission from a mode I crack tip is given by equation(1)[4]

$$K_{Ic} = \frac{2}{\sin \phi \cos\left(\frac{1}{2}\phi\right)} \left\{ \frac{\mu b}{(1-\nu)(8\pi r_c)^{1/2}} + (2\pi r_c)^{1/2} \left(\sigma_f + \frac{4\gamma e^{1/2} \sin \phi}{\pi r_c (1+e^3)} \right) \right\}, \quad (1)$$

where b is the Burgers vector, μ the shear modules, ν the Poisson's ratio, σ_f the lattice friction stress, $r_c = d/e$ [5] the core radius of the dislocation and d the spacing of slip planes, and Φ an inclination angle. $\Phi = 70^\circ$ was used here, because it corresponds to the minimum K_{Ic} . The values of surface energy γ , Burgers vector b , etc. used in this calculation were taken from ref. [4], [6] and [7]. The yield strength of the aluminium single crystal is chosen as the friction stress σ_f , i.e., $\sigma_f = 20 \text{ MPa}$ [4]. Substituting all data into Eq.(1), we have $K_{Ic} = 0.65 \text{ MPa}\sqrt{m}$.

The shear modulus μ relates to the surface energy, γ , in the following way [8]

$$\gamma = \frac{Ea^2}{\pi^2 d} = \frac{2\mu(1+\nu)a^2}{\pi^2 d}, \quad (2)$$

where a is the distance between atoms. The surface energy of aluminium can be decreased by chemisorption of Hg atoms from $\gamma = 1.14 \text{ J/m}^2$ to $\gamma(L) = 0.35 \text{ J/m}^2$ [7]. Thus, the localized shear modulus in the region of the crack tip would decrease from $\mu = 26.3 \text{ GPa}$ to $\mu(L) = [\gamma(L)/\gamma]\mu = 8.1 \text{ GPa}$. In general, chemisorption of liquid metal does not induce any change in σ_f , Φ , r_c and b . Substituting $\gamma(L) = 0.35 \text{ J/m}^2$ and $\mu(L) = 8.1 \text{ GPa}$ into Eq. (1) leads to $K_{Ic}(L) = 0.17 \text{ MPa}\sqrt{m}$. This reveals that chemisorption of Hg atoms reduces the critical stress intensity for dislocation emission from $K_{Ic} = 0.65 \text{ MPa}\sqrt{m}$ to $K_{Ic}(L) = 0.17 \text{ MPa}\sqrt{m}$.

For a TEM foil specimen, the ledge energy of the surface step produced by a screw ledge component of the dislocation is a resistance to dislocation motion. The decrease in the surface energy, due to chemisorption of Hg atoms on the specimen surface, decreases the resistance to dislocation motion. The resistance to move a screw dislocation lying perpendicular to the foil is given by Eq.(3)[9]

$$\sigma_{yz}^* = \frac{2\gamma}{L} + \sigma_f. \quad (3)$$

Let L be 100 nm , which is a reasonable thickness for a TEM foil, using yield strength of aluminium as the value for lattice friction, i.e. $\sigma_f = 20 \text{ MPa}$. From Eq.(3) we obtain $\sigma_{yz}^* = 42.8 \text{ MPa}$ and $\sigma_{yz}^*(L) = 27 \text{ MPa}$, which correspond to the resistance before and after the chemisorption of Hg atoms on the specimens surface.

2. Chemisorption-Facilitated Dislocation Emission, Motion Resulting in the Initiation of LMICs

Sleeswyk has proposed a dislocation model for continuous propagation of a sharp crack in liquid metal medium [10]. Our results, however, show that LMICs could be nucleated continuously at crack tip and/or discontinuously in the DFZ only when chemisorption-facilitated dislocation emission and motion reached to a critical condition. Experimental results show that a DFZ was formed between the loaded crack tip and the dislocation pile-up before initiation of LMICs. The DFZ formed elastically, while the plastic deformation around it shields the applied stress intensity. Dislocation emission blunts the crack tip. A detailed finite element method calculation of discrete dislocations indicated the emergence of two stress peaks ahead of the blunted crack tip, as the dislocation piles up against the DFZ [11]. One of the stress peaks is at the crack tip and the other is in the DFZ. Atomic bonds will break when one or both of the peaks exceeds the cohesive strength, resulting in initiation of nanocrack in the DFZ or at the blunted tip.

3. Chemisorption-Lowered the Surface Energy Resulting in the Reduction of Fracture Toughness

The crack tip is blunted into a notch with the radius ρ after dislocation emission from the crack tip. The stress at the notch tip is given by [12]

$$\sigma_Y = \frac{2K_I}{\sqrt{\pi\rho}} = 2\sigma\sqrt{\frac{c}{\rho}} \quad (4)$$

where c is the crack length. When σ_Y is equal to the cohesive strength, $\sigma_{th} = (E\gamma/a)^{1/2}$ [13] (where a is the atomic spacing of fracture plane), a microcrack would nucleate at the crack tip and propagate. The fracture stress σ_c , can be obtained by

$$\sigma_c = \left(\frac{E\gamma\rho}{4ac} \right)^{1/2} \quad (5)$$

Fracture stress, σ_c can also be obtained according to Orowan's theory in [12], i.e.,

$$\sigma_c = \sqrt{\frac{E(2\gamma + \gamma_p)}{\pi c}} = \sqrt{\frac{2E\gamma_{eff}}{\pi c}} \quad (6)$$

Combining Eqs.(5) and (6), we have the effective surface energy γ_{eff}

$$2\gamma_{eff} = 2\gamma + \gamma_p = \left(\frac{\pi\rho}{4a} \right) \gamma \quad (7)$$

Since 2γ is much less than γ_p and could be neglected in Eq.(7), γ_p can be expressed as a function of γ as

$$\gamma_p = \left(\frac{\pi\rho}{4a} \right) \gamma \quad (8)$$

Chemisorption of liquid metal atoms causes the surface energy to decrease from γ to $\gamma(L)$, and then decrease effective surface energy from γ_{eff} to $\gamma_{eff}(L)$ i.e.,

$$2\gamma_{eff}(L) = \left(\frac{\pi\rho}{4a} \right) \gamma(L) \quad (9)$$

Fracture toughness tested in air and in liquid metal medium K_{IC} and $K_{IC}(L)$ can be expressed as [2]

$$K_{IC}^2 = E(2\gamma + \gamma_p) = 2E\gamma_{eff}, \quad K_{IC}^2(L) = 2E\gamma_{eff}(L) \quad (10)$$

Combining Eqs.(9) and (10) leads to

$$\frac{K_{IC}^2(L)}{K_{IC}^2} = \frac{2\gamma_{eff}(L)}{2\gamma_{eff}} = \frac{\gamma(L)}{\gamma} \quad (11)$$

There is no contradiction between chemisorption-facilitated dislocation emission, motion and chemisorption-decreased plastic works. Localized plastic deformation can occur under a lower applied stress because of chemisorption of liquid metal. On the other hand, chemisorption-facilitated dislocation emission and motion can make the plastic deformation more localized, thus the size of the plastic deformation zone can be decreased. So the plastic work would also be decreased by chemisorption of the liquid metals.

5. CONCLUSIONS

1. Chemisorption of Hg atoms on a loaded crack surface of Al single crystal facilitated dislocation emission, multiplication and motion.

2. LMIC was nucleated at the crack tip or in the DFZ only when chemisorption-enhanced dislocation emission and motion was developed into a critical degree.

3. Chemisorption of liquid metal could decrease the critical stress intensity factor for dislocation emission, K_{IC} , the resistance to dislocation motion, and the plastic work γ_p , via the reduction of surface energy, resulting in the facilitating dislocation emission and motion and lowering fracture toughness.

ACKNOWLEDGMENT: This work is partially supported by the National Natural Science Foundation of China and partially supported by the Hong Kong Research Grants Council through RGC grant HKUST 819/96E.

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