Liquid metal embrittlement mechanism*

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Abstract   Liquid metal embrittlement was studied in the following two aspects. First the first principle and Chen-Nanxian three-dimensional lattice reverse method were employed to obtain the effective potentials for Al-Ga and Ga-Ga. Then with the molecular dynamics simulation, the influence of liquid metal adsorption on dislocation emission was studied. The simulated result shows that after Ga atoms are adsorbed on the crack plane in Al crystal, the critical stress intensity factor decreases, which changes from 0.5 MPam$^{1/2}$ (without adsorption) to 0.4 MPam$^{1/2}$ (with adsorption). The reason for the reduction in the critical intensity stress factor is that Ga adsorption reduces the surface energy of the crack plane. Moreover, 7075 Al alloy adsorbing liquid metal (Hg + 3atm% Ga) was *in-situ* studied in TEM by using a special constant deflection device. The experimental result showed that liquid metal adsorption could facilitate emission, multiplication and motion of dislocations. When this process reached a critical condition, the brittle microcrack was initiated and propagated from the crack tip or in a dislocation free zone.

Keywords: molecular dynamics, stress intensity factor, Ga, liquid metal embrittlement, TEM, 7075 Al alloy.

Currently there are a lot of different viewpoints on the mechanism of brittle fracture induced by liquid metals[1—4]. It is generally understood that adsorption decreases surface energy (or bond strength), then causes materials to fail[2—4]. We once made some experiments on 7075 aluminum alloy. The results showed that the critical stress intensity factor for crack nucleation was $K_{IC}(L) = 1.7$ MPam$^{1/2}$. This value is one order of magnitude lower than the fracture toughness $K_{IC} = 43$ MPam$^{1/2}$ of 7075 aluminum alloy. Substituting the K_{IC} value into Orowan's equation $K_{IC}^2 = 2\gamma_{eff} \cdot E/(1 - \nu^2)$, the effective surface energy $2\gamma_{eff}$ was calculated to be $2\gamma_{eff} = 37$ J/m^2. But the calculated value is also one order of magnitude greater than the real surface energy $\gamma = 1.15$ J/m^2 of aluminum. Hence, the plastic work γ_p is the main item of the resistance to fracture $R = 2\gamma_{eff} = 2\gamma + \gamma_p$ in the process of metal fracture. That is to say, there is localized plastic deformation in brittle failure induced by the adsorption of the liquid metals. Previously Lynch proposed that liquid metals adsorbed on the crack surface, just like hydrogen, will decrease surface energy and enhance localized plastic deformation, then result in brittle fracture[5]. The viewpoint, however, has not been tested directly by experiments.

By *in-situ* TEM observations, Su and his co-workers' result showed that liquid metals

adsorbed on the crack surface in Al crystal could facilitate dislocation emission, multiplication and motion. When dislocation emission and motion reaches a critical condition, brittle microcracks nucleate[6]. It is important to study liquid metal induced dislocation emission and motion by using molecular dynamics simulation and TEM direct observation.

Up to now, the potential for Hg is not available. We developed an inversion method to obtain the potentials for Al-Ga and Ga-Ga[7]. Moreover, because the sensitivity of brittle fracture of Al induced by Ga is quite high, the system Al-Ga is used in this calculation.

It is a new method that liquid metal embrittlement is studied from the point of view of dislocations. The most direct approach for investigating dislocation emission, multiplication and motion is *in-situ* TEM tension. Here a special TEM loading device was designed to study dislocation configuration ahead of a crack tip induced by various media, such as chemical solution and liquid metals[8,9]. Our macroscopic experiments showed that 7075 alloy fractured under low stress in liquid metal Ga[5]. The bulk specimen adsorbing Hg cracked intergranularly. In this paper, by *in-situ* TEM observation, 7075 alloy was used to study the influence of liquid metal adsorption on dislocation emission, multiplication and motion.

1　Experimental procedures

The material used in this investigation was 7075 (LC4) Al alloy. The specimens were kept at 475℃ for 1 h, followed by water quenching, and then tempered at 135℃ for 15 h. 0.02 mm thick foil specimens were cut by a spark machine from the bulk material. First the sheets were ground by emery paper to about 100 μm in thickness. Then the specimens were thinned by double jet electropolishing in the solution of 10% $HClO_4$ + 90% CH_3CH_2OH until small holes were formed. After these processes, ion bombardment was used to clean the surface and remove hydrogen induced by electropolishing.

The foil specimens were mounted on the special constant deflection device[8,9]. A stress was applied with a screw until cracks appeared around the holes and the specimens were put in a desiccator for 20—24 h. After the dislocation configuration ahead of the crack tip was examined, the specimen was crept in TEM for 0.5—1 h. If the dislocation configuration did not change with time any more, it indicated that the creep reached a stable status at room temperature.

The pre-crept specimen with the loading set was put above liquid surface of Hg + 3atm% Ga in a closed container. After the adsorption lasted for a given time, we put the foil specimen in TEM, and observed changes of the dislocation configuration ahead of the crack tip and the initiation of microcracks.

2　Experimental results

Specimen 1 was loaded by the constant deflection device until dislocations were emitted from the crack tip. Its displacement was kept constant and it was pre-crept in a desiccator for 24 h, then observed in TEM continuously. The dislocation configuration ahead of the crack tip did not change. This indicated that the dislocation configuration reached a stable state, as shown in fig. 1(a). Putting the loading set with the specimen above liquid metal of Hg + 3atm% Ga for 30 min and 1 h, respectively, no change in the dislocation configuration was found by TEM observation, as shown in fig. 1(b). This indicated that careful experimental operation and short time adsorption did not cause any dislocation emission and motion. After the specimen was put above liquid

metal for about 6 h, the dislocation configuration changed dramatically, as shown in fig. 1(c). Comparing fig. 1(c) with fig. 1(b), we can see that the dislocation density in region CDEF increased obviously, and a new set of dislocations was formed in a region BC. Because the dislocations in the region BC were laid ahead of the crack tip, they must be emitted from the crack tip A. The increment in dislocation density in the region CDEF originated from dislocations newly emitted from the crack tip or multiplication of the dislocation source. This showed that adsorption of liquid metal, under low loading, can facilitate dislocation emission.
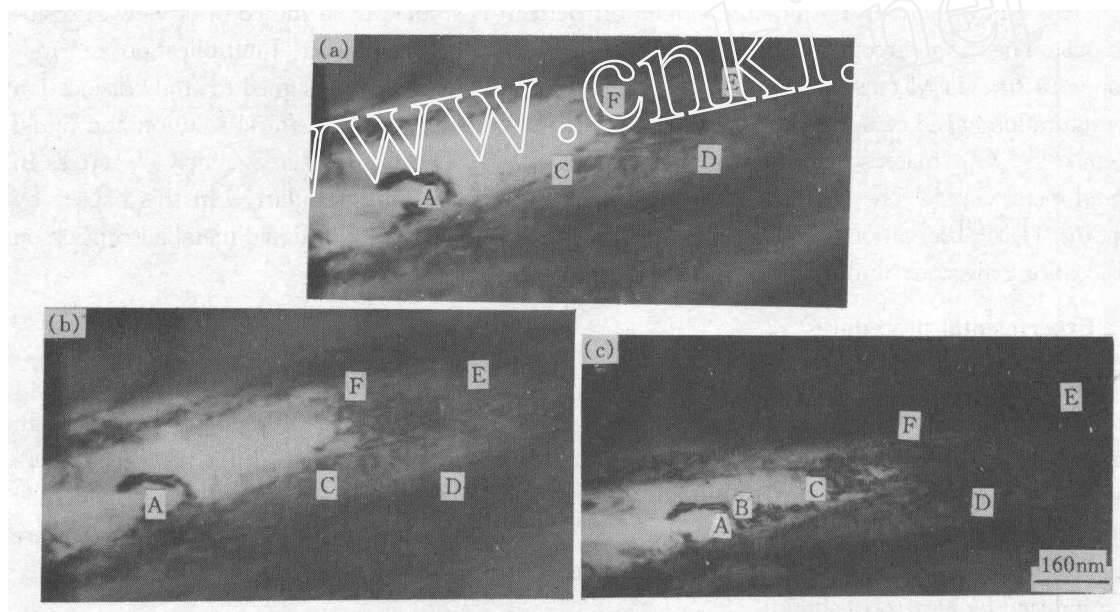

Fig. 1.   Effect of metal adsorption on emission and multiplication of dislocations. (a) Original dislocation status in front of a pre-loaded crack tip after 24 h creeping in air; (b) 1 h in Hg + 3% Ga atmosphere; (c) 6 h in Hg + 3% Ga atmosphere.

Specimen 2 was pre-crept for 22 h, then crept in TEM for 0.5 h. The dislocation configuration before the crack tip was shown in fig. 2(a). Putting the specimen above liquid metal for 6 h, we observed that dislocations in the region DE had moved beyond the view field, and meanwhile dislocations in the region BC moved, as shown in fig. 2(b). Specimen 3 was pre-crept for 20 h, then crept in TEM for 0.5 h until the dislocation configuration reached a stable state, as shown in fig. 3(a). Putting it above liquid metal for 5 h, dislocation configuration changed, as shown in fig. 3(b). Many new dislocations were formed in BC ahead of the crack tip A. Continuously
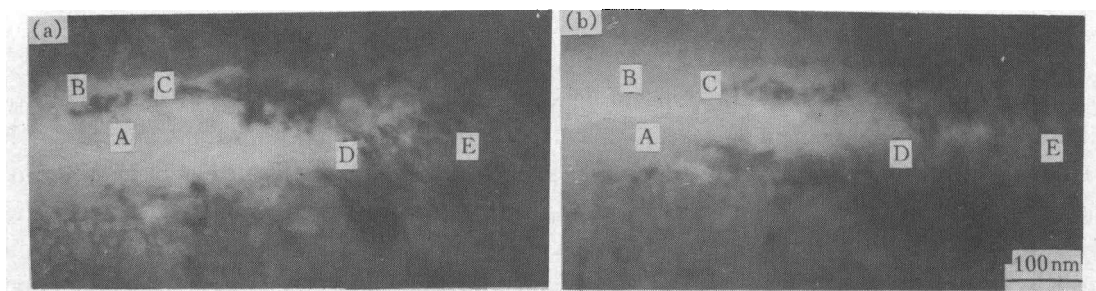

Fig. 2.   Enhancement of metal adsorption on dislocation movement. (a) A status pre-crept 22 h; (b) 6 h in atmosphere of the liquid Hg + 3% Ga.

putting it above liquid metal for 2 h, dislocations were emitted, multiplied and moved. Moreover, a DFZ indicated by BCD was formed ahead of the crack tip, but microcracks were not initiated yet, as shown in fig. 3(c). This means that liquid metal adsorption in the crack tip can enhance dislocation emission, multiplication and motion. Previous study showed that the adsorption of Ga on the crack surface in pure Al (loading speci-mens were put above liquid of Ga at 50℃) could also facilitate dislocation emission, multiplication and motion.

3   Theoretical calculation

3.1   Procedure of molecular dynamics simulation

The interactive pair potential between Al and H can be obtained from *ab initio* calculation and the Chen-Mobius 3D lattice inversion formula. Then the interactive pair potential was used to investigate the influence of H on dislocation emission in Al crystal[7]. Similarly, the interaction potentials for Al-Ga and Ga-Ga can be calculated. The parameters in the Rose's equation of state, i. e. bulk module B, equilibrium energy E_0 and lattice constant a_0 can be figured out from the first principle calculation. Values of B, E_0 and a_0 are listed in table 1. The pair potentials for Ga and Al-Ga are illustrated in fig. 4. The N-body potential for Al was used[10].

In FCC crystals, a full dislocation moves on the $\{111\}$ plane in the $\langle110\rangle$ direction. In the present model, the paper plane was set to be $(11\bar{2})$ plane, which was used as the projected plane. The purpose is to observe easily the emit-ted Schockley dislocations. The inclination angle
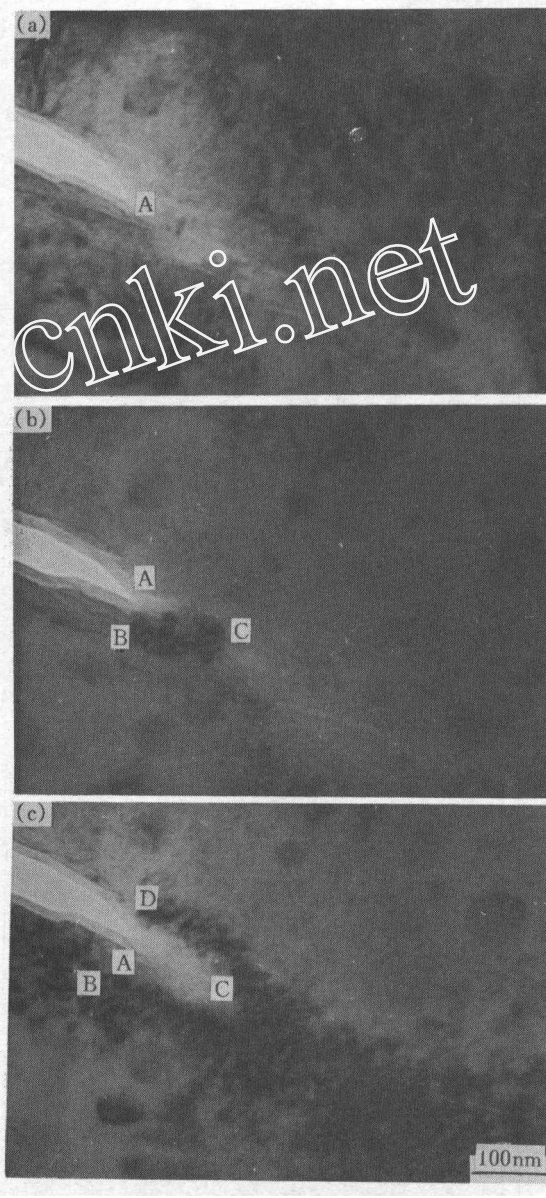

Fig. 3.   Enhancement of metal adsorption on dislocation emission, multiplication and movement. (a) An original status pre-crept in air for 20 h; (b) 5 h in atmosphere of the liquid Hg + 3% Ga; (c) 7 h in atmosphere of the liquid Hg + 3% Ga.

of the slip plane with respect to the crack plane is set to be $70°$. x, y, z axes are along $[13\,5\,9]$, $[19\overline{35}\,\overline{8}]$ and $[11\bar{2}]$, respectively. The length in x-direction is $35a_0$, in y-direction $40a_0$ and in z-direction $\frac{\sqrt{6}}{12}a_0$(one period). The total atom number is 6 640. The loading direction is in y-direction, so the crack is mode I. The boundary conditions applied to the boundary of the discrete atom region in the simulation are dictated by a mode I anisotropic K field in the x-y plane. In the z-direction, a six-layer periodic representation is applied. The time step is $\Delta t = 0.005$ ps. The

temperature of the model is set to be 100 K. Calculation details are similar to those in reference [7].

<center>Table 1   Values of B, E_0 and a_0 calculated from the first principle</center>

	$B \times 10^{11}/\mathrm{N \cdot m^{-2}}$	$E_0 \times 1.60 \times 10^{-9}/\mathrm{J}$	$a_0 \times 10^{-10}/\mathrm{m}$
Al	0.742	3.835	4.101
Ga	0.805	3.220	4.169
AlGa	0.686	3.149	3.235
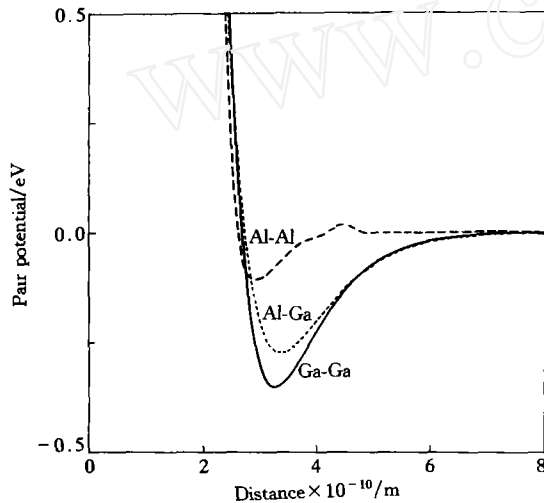
Fig. 4.   Pair potentials of Ga and Ga-Al.

3.2   Simulated results and discussion

For pure Al crystal, when the applied stress intensity factor is $K_I = 0.5$ MPam$^{1/2}$, the first partial dislocation was emitted. It moved in the plane (111) (see fig. 5(a)). It means that the critical stress intensity factor of the crack in mode I in Al crystal was $K_{Ie} = 0.5$ MPam$^{1/2}$. If Ga atoms are adsorbed on the crack plane, only when the stress intensity factor is $K_I = 0.4$ MPam$^{1/2}$, a partial dislocation will be emitted from the crack tip, as shown in fig. 5(b). That is to say, if Ga atoms are adsorbed on the crack plane, the critical stress intensity factor will reduce from $K_I = 0.5$ MPam$^{1/2}$ to $K_I = 0.4$ MPam$^{1/2}$, which decreases by 20%. When load was applied further, the partial dislocations emanated from the crack tip unceasingly. At the same time, a step "abcdef" appeared ahead of the crack tip, as shown in fig. 6(a). Adsorbed Ga atoms can change the atomic configuration ahead of the crack tip. A vacancy cluster was produced, as indicated by "A" in fig. 6(b). Because there exist super-saturated vacancies, one Frank dislocation ($b = [111]/3$) was produced near the crack tip, as indicated by "B" in fig. 6(b). Schockley dislocations will also be emitted from the crack tip.

(a)   (b)
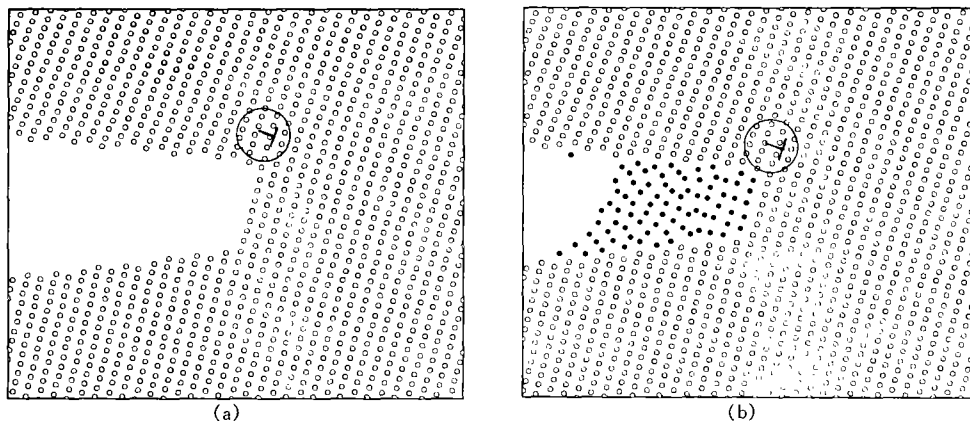
Fig. 5.   Effect of Ga adsorption on critical stress intensity factor for dislocation emission. (a) First emitted dislocation at 0.5 MPam$^{1/2}$ without Ga adsorption; (b) first emitted dislocation at 0.5 MPam$^{1/2}$ with Ga adsorption.
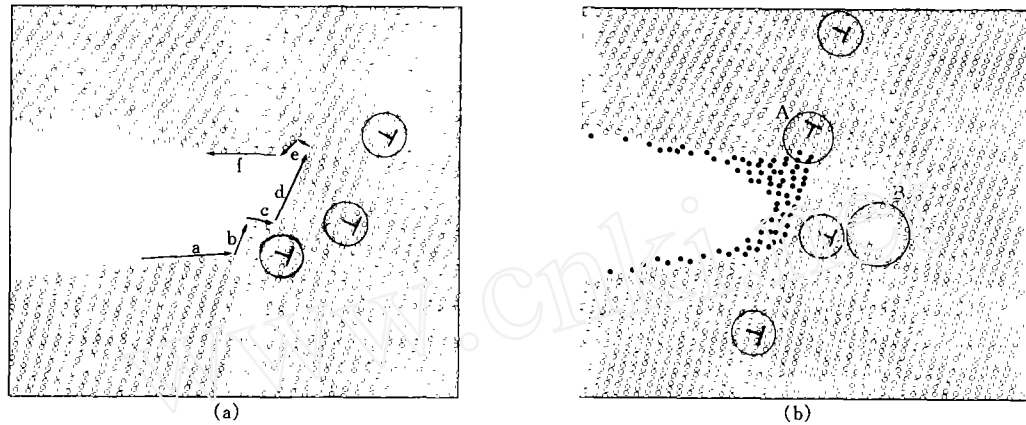
Fig. 6. Effect of Ga adsorption on configuration of Al atoms around the crack tip. (a) $K_I = 1.1$ MPam$^{1/2}$ without Ga adsorption; (b) $K_I = 1.1$ MPam$^{1/2}$ with Ga adsorption.

The reason that absorbed metal atoms can reduce the critical stress intensity for dislocation emission is related to surface energy. The critical stress intensity factor for dislocation emission under mode I crack can be expressed as[11]

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

where ϕ is an angle between the crack plane and the dislocation slip plane, μ the shear modulus, b Burgers' vector, ν Poison ratio, r_c the radius of a dislocation core, γ the surface energy and σ_f lattice resistant, which is P-N force for a perfect crystal. For Al crystal, the values of the parameters are $r_c = d/c$, and the angle ϕ is 70°, $b = 1.65 \times 10^{-10}$ m, $\mu = 26.3$ GPa, $\nu = 0.34$, $\sigma_f = 10^{-5} \mu$. σ_f is small enough to be neglected. Substituting all the data into eq. (1), K_{Ie} is calculated to be 0.38 MPam$^{1/2}$. There is relationship between μ and γ[12]:

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

where a is the lattice constant, $d = \frac{\sqrt{6}}{3}a_0$ is the effective distance of crystal plane. The data for Hg is used as a sample here. Hg adsorption will decrease surface energy for Al from $\gamma = 1.15$ J/m^2 to $\gamma = 0.35$ J/m$^{2[4]}$. From eq. (2) we get $\mu(L) = \mu\gamma(L)/\gamma = 0.304 \mu = 8.0$ GPa. Substituting the value of μ_L into eq. (1), $K_{Ie(L)}$ is calculated to be 0.114 MPam$^{1/2}$. Because of lack of surface energy for Al with Hg adsorption, we cannot carry on quantitative calculations.

4 Conclusion

1) The adsorption of liquid metal on the crack plane in 7075 aluminum alloy can facilitate dislocation emission, multiplication and motion.

2) The molecular dynamics simulation showed that Ga adsorption on Al crack plane decreased the critical stress intensity from 0.5 MPam$^{1/2}$ to 0.4 MPam$^{1/2}$, and liquid metal adsorption would facilitate dislocation emission.

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