[Paper]

First-Principles Study on Twin Generation Induced by Symmetry Breaking in Cu-In Alloy

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We investigated deformation twinning in Cu-In alloy with even distribution of In atoms through density functional theory (DFT) calculations. Twinnability of Cu-In alloy were evaluated based on the general stacking fault energies (GSFE) and compared with those of pure Cu, Cu-Al, and Cu-Zn alloys. Cu-In alloy demonstrated a substantial reduction in stacking fault energies. Especially, the twinnability is significantly enhanced along a specific path among six available partial slip directions, owing to the symmetry-breaking effect induced by In atoms. The local lattice strain by In atoms in Cu matrix led to more pronounced symmetry breaking compared to Al and Zn, thereby facilitating twin formation in specific directions. Since the local lattice strain is randomly distributed in the grain, the energy barrier to generate a twin can be lowered in all directions, accelerating twin formation throughout the grain.

Keywords: *Cu-In alloy, deformation twin, twinnability, density functional theory, Cu-Al alloy, Cu-Zn alloy*

1. Introduction

The formation of deformation twins (DTs) is known to be highly dependent on the stacking fault energy (SFE) of metals. In pure copper, it is difficult to generate DTs due to the relatively high SFE of about 50 mJ/m^2 [1]. Although Al and Zn can reduce the SFE of Cu, it is not easy to obtain a high density of DTs without severe plastic deformation (SPD) processing in Cu-Al and Cu-Zn alloys.

Recently, Cu-In alloy with high-density DTs were fabricated through normal deformation process, showing the excellent tensile strength of about 1.3 GPa[2]. The previous first-principles calculations revealed that the SFE can be more effectively lowered on the Cu (111) slip plane doped with an In atom compared to Al and Zn[3]. However, although the average In concentration ranged from 2 to 10 at.% in the simulation models, the In concentration of each Cu (111) plane had only one of two values, 0 and 25 at.%, showing a substantial deviation from experimental conditions. And the average twinnablity in Cu-In alloy was poorer than that of Cu-Al or Cu-Zn alloys, which did not match the experimental results.

In this study, the density functional theory (DFT) simulations were performed to investigate the effect of In atoms on twin generation in Cu-In alloy with even distribution of In atoms. The previous atomic model with 48 Cu atoms was scaled up to 192 Cu atoms to set the same In concentration of 6.25 at.% at each Cu (111) plane, similar to the experimental conditions[2].

2. Calculation Method

We performed first-principles calculations based on the DFT. The projector augmented wave (PAW) pseudopotentials[4)5] were expanded with a cutoff energy of 450eV. We used the Perdew-Burke-Ernzerhof approximation[6] for the exchange-correlation potential as implanted in the Vienna Ab-initio Simulation Package code (VASP)[7)8].

To calculate the general stacking fault energies (GSFE) and twinnability of Cu alloys, we used a (4x4x4) Cu slab structure, which consisted of 192 atoms as shown in Fig. 1. It has 12 layers of Cu (111) planes with a vacuum of 15 Å in order to avoid interactions between adjacent slabs. We use (2x2x1) k-points in the Brillouin-zone. A single alloying atom, such as In, Al and Zn, is placed on each Cu (111) plane (6.25 at.%), while these

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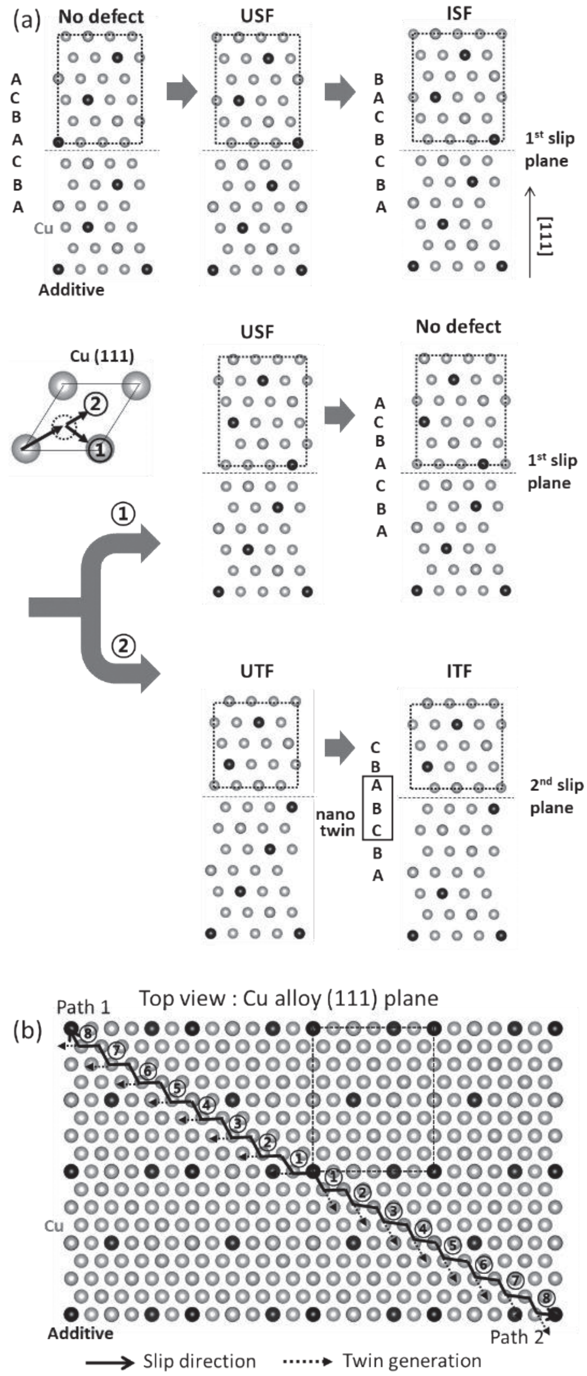

Fig. 1 (a) Atomic models of Cu alloys with no defect, unstable stacking fault (USF), intrinsic stacking fault (ISF), unstable twin fault (UTF) and intrinsic twin fault (ITF), respectively. (b) Atomic model of Cu (111) plane. Two partial slip directions (Path 1 and 2) are denoted by arrows.

additive elements are away from each other enough to minimize the interaction between them. To reduce the residual forces on each atom below 0.01eV/Å, we employed the conjugate-gradient method. During atomic relaxation, the position of all atoms belonging to two (111) layers near the surface of the Cu slab were fixed.

Three mode of twinnability, such as the orientation, crack tip and grain boundary modes (T_{OR}, T_{CT} and T_{GB})[9)~11)], are evaluated as

$$T_{OR} = \arctan\left(\frac{\gamma_{utf}/\gamma_{usf}-1}{\gamma_{isf}/\gamma_{usf}-1}\right)+\frac{\pi}{4}$$

$$= \arctan\left(\frac{\beta-1}{\alpha-1}\right)+\frac{\pi}{4} \quad (1)$$

$$T_{CT} = \left[1.136-0.151\frac{\gamma_{isf}}{\gamma_{usf}}\right]\sqrt{\frac{\gamma_{usf}}{\gamma_{utf}}}$$

$$= [1.136-0.151\alpha]/\sqrt{\beta} \quad (2)$$

$$T_{GB} = \sqrt{\frac{3\gamma_{usf}+2\gamma_{isf}}{\gamma_{utf}}} = \sqrt{(3+2\alpha)/\beta} \quad (3)$$

where γ_{usf}, γ_{isf} and γ_{utf} are the unstable stacking fault energy, the intrinsic stacking fault energy and the unstable twin fault energy, respectively, while the parameters of α and β represent $\gamma_{isf}/\gamma_{usf}$ and $\gamma_{utf}/\gamma_{usf}$, respectively.

The stacking fault energies (SFE) of γ_{usf}, γ_{isf} and γ_{utf}, can be obtained from the generalized stacking fault energy (GSFE) curves. To generate a GSFE curve and extract these SFE, a 12-layer Cu slab with solute atoms such as In, Al and Zn was used as shown in Fig. 1 (a). The top 6 layers were shifted along <112> direction until the intrinsic stacking fault (ISF) was generated at the first slip plane, and then the top 5 layers were moved in a similar way to form the intrinsic twin fault (ITF), which corresponds to a 2-layer nano-twin. The unstable stacking fault (USF) and unstable twin fault (UTF) are the atomic arrangements corresponding to the local maxima in the GSFE curve, respectively.

The face centerd cubic (FCC) structure of copper has six equivalent <112> partial slip directions on the (111) plane. The simulation model of Cu alloys has a 8 times elongated Burger's vector due to the configuration of the alloying atoms as shown in Fig. 1 (b). In this study, the GSFE along two slip directions (Path 1 and 2 in Fig. 1 (b)) were computed and used to evaluate averaged twinnability.

3. Result and Discussion

3.1 The stacking fault energies (SFE) of Cu-In alloy

Fig. 2 shows the SFE of γ_{isf}, γ_{usf}, γ_{utf} and γ_{itf} at each step along path 1 and 2 for pure Cu, Cu-Zn, Cu-Al and Cu-In alloys. In general, the SFE on the Cu (111) plane with an additive atom of Zn, Al or In were lower than that of pure Cu for both paths 1 and 2. The SFE reduction was the largest for Cu-In alloys. The spacing between pure Cu (111) slip planes is 2.08Å, while it is 2.10, 2.11, or 2.13 Å for Cu-Zn, Cu-Al or Cu-In alloys, respectively. The repulsive interactions caused by the

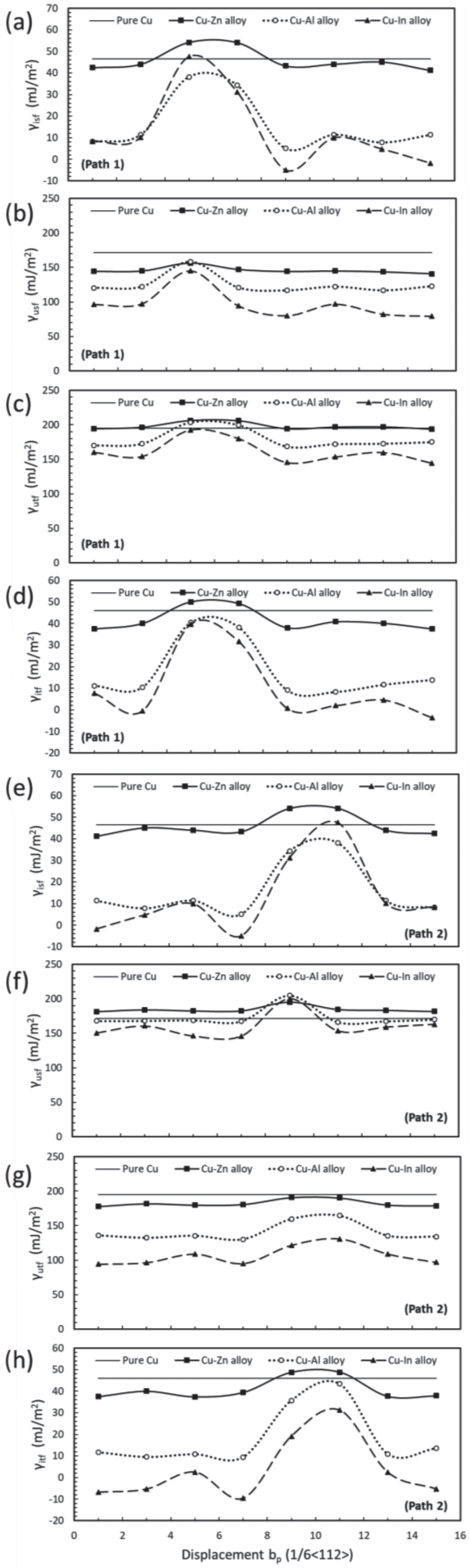

Fig. 2　The stacking fault energies of (a) γ_{isf}, (b) γ_{usf}, (c) γ_{utf} and (d) γ_{itf} along path 1 and (e) γ_{isf}, (f) γ_{usf}, (g) γ_{utf} and (h) γ_{itf} along path 2 for pure Cu, Cu–Zn, Cu–Al and Cu–In alloys.

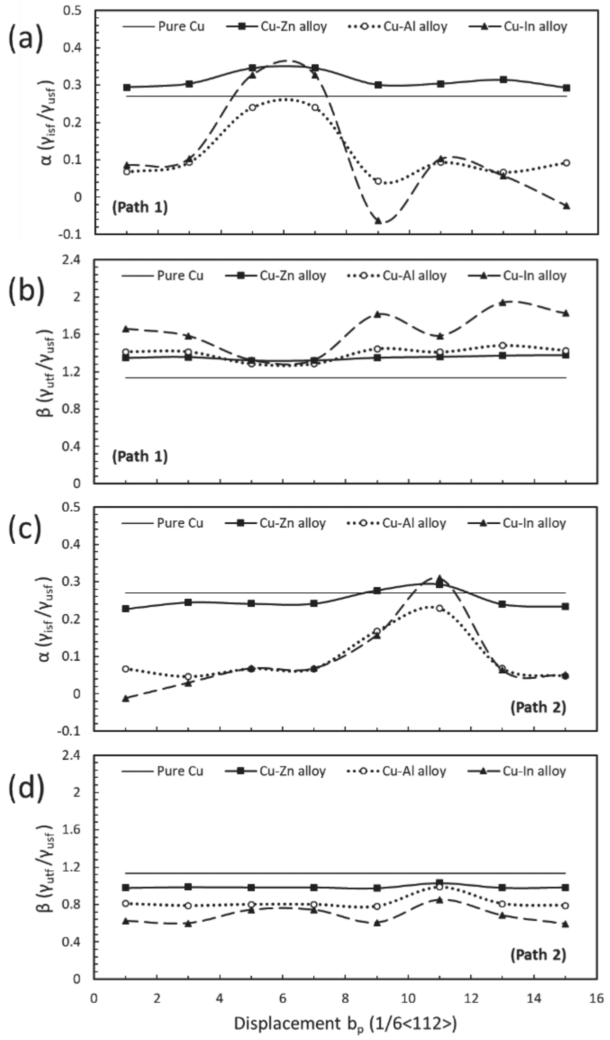

Fig. 3　The parameters of (a) $\alpha = \gamma_{isf}/\gamma_{usf}$ and (b) $\beta = \gamma_{utf}/\gamma_{usf}$) along path 1 and (c) α and (d) β along path 2 for pure Cu, Cu–Zn, Cu–Al and Cu–In alloys.

charge overlap of Cu and solute atoms weaken the bonding force of atoms in two adjacent (111) slip planes, resulting in a decrease in SFE. Since the distance between the (111) planes with In atoms is the widest, the bonding force between atoms in these slip planes is the most effectively weakened, resulting in the largest reduction of the SFE in Cu–In alloy, compared to the case of Al and Zn. The result is in good agreement with previous work[3]. The SFE suddenly increases at a certain step because the distance between two solute atoms on the (111) planes becomes closer during slipping, causing severe lattice strain.

In Fig. 3, the parameters of α ($= \gamma_{isf}/\gamma_{usf}$) and β ($= \gamma_{utf}/\gamma_{usf}$) are shown at each step along path 1 and 2 for pure Cu, Cu–Zn, Cu–Al and Cu–In alloys. The α and β indirectly represent the energy barrier to create stacking faults and twins, respectively. When Cu (111) slip planes are doped with solute atoms, such as In, Al and Zn, the value of α is lowered for both paths 1 and 2.

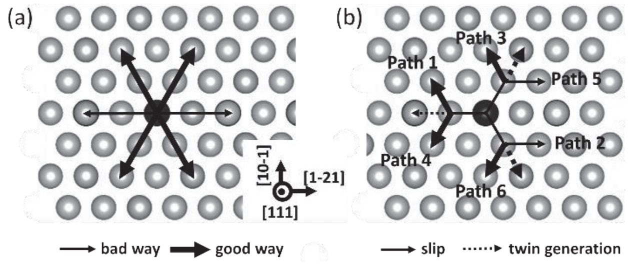

Fig. 4 (a) Six <112> partial slip directions. The partial slip occurs better in the direction pointed by a thick arrow than by a thin arrow. (b) Six available slip paths through partial slip under <110> external stress.

However, the β shows completely different patterns for paths 1 and 2. The β of Cu alloys is higher than that of pure Cu for path 1, while it is lower for path 2. It means that deformation twins are likely to occur along path 2, not path 1.

The reason for the specific slip direction favoring twin formation is the broken FCC symmetry by the additive atoms. The lattice constant in the [10-1] direction increases by 1.6%, 1.5%, and 3.2% for Cu-Zn, Cu-Al, and Cu-In alloys, respectively, compared to pure copper, while in the [1-21] direction, it changes by less than 0.5%. As depicted in Fig. 4 (a), the partial slip occurs more easily in four slip directions, where atom spacing has widened, among six <112> slip directions. Consequently, among the six possible slip paths in Fig. 4 (b), paths 1 and 4 prefer the formation of a trailing partial dislocation, and paths 2 and 5 prefer the twin generation. For paths 3 and 6, the formation of twins and trailing partial dislocations compete with each other. Among the additives, In atoms causes the largest lattice distortion and therefore the most symmetry-breaking effect.

3.2 The averaged SFE of Cu-In alloy

Deformation twins are very likely to form in particular directions when the local lattice strain induced by the additive elements breaks the FCC symmetry. However, since the additive atoms are randomly distributed in experiments, it is unlikely that the symmetry is broken in a consistent direction over the grain. To evaluate the actual twinnability, we calculated the average value of SFEs obtained from paths 1 and 2, which favors the formation of a trailing partial dislocation and twin, respectively.

Fig. 5 shows the averaged values of the stacking fault energies (SFE) of γ_{isf}, γ_{usf}, γ_{utf} and γ_{itf} and the parameters of α and β for pure Cu, Cu-Zn, Cu-Al and Cu-In alloys. The average SFE decreases in the order of Cu-Zn, Cu-Al, and Cu-In alloys. In particular, the energy of intrinsic twin fault (γ_{itf}) in Cu-In alloy is less than 10 mJ/m^2,

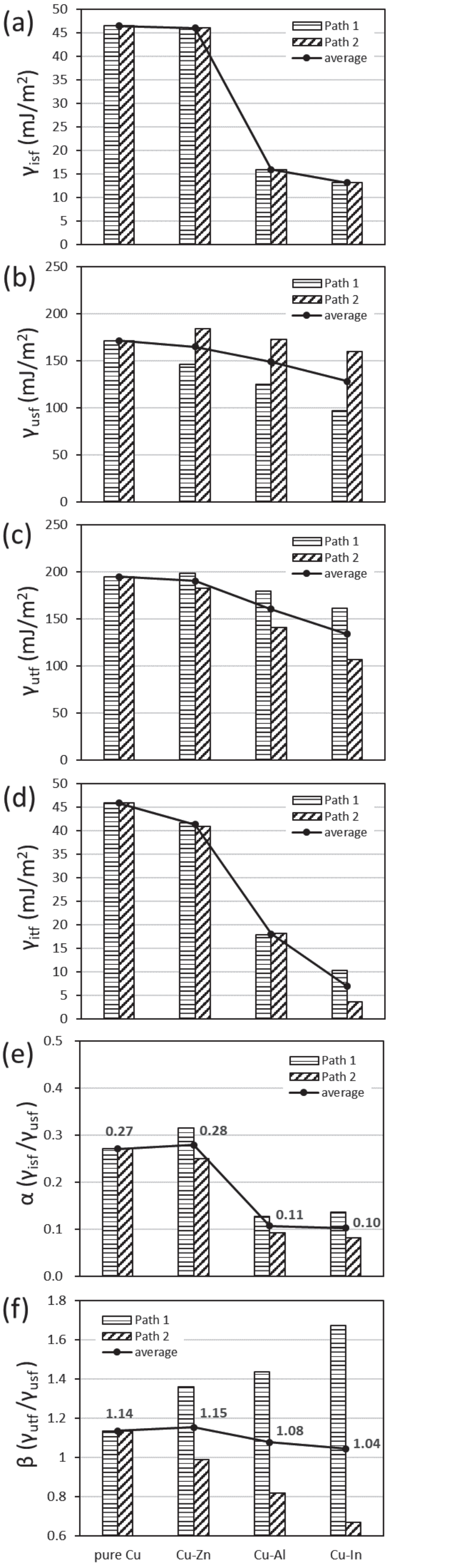

Fig. 5 The averaged stacking fault energies of (a) γ_{isf}, (b) γ_{usf}, (c) γ_{utf} and (d) γ_{itf} and the parameters of (e) $\alpha=\gamma_{isf}/\gamma_{usf}$ and (f) $\beta=\gamma_{utf}/\gamma_{usf}$ for pure Cu, Cu-Zn, Cu-Al and Cu-In alloys.

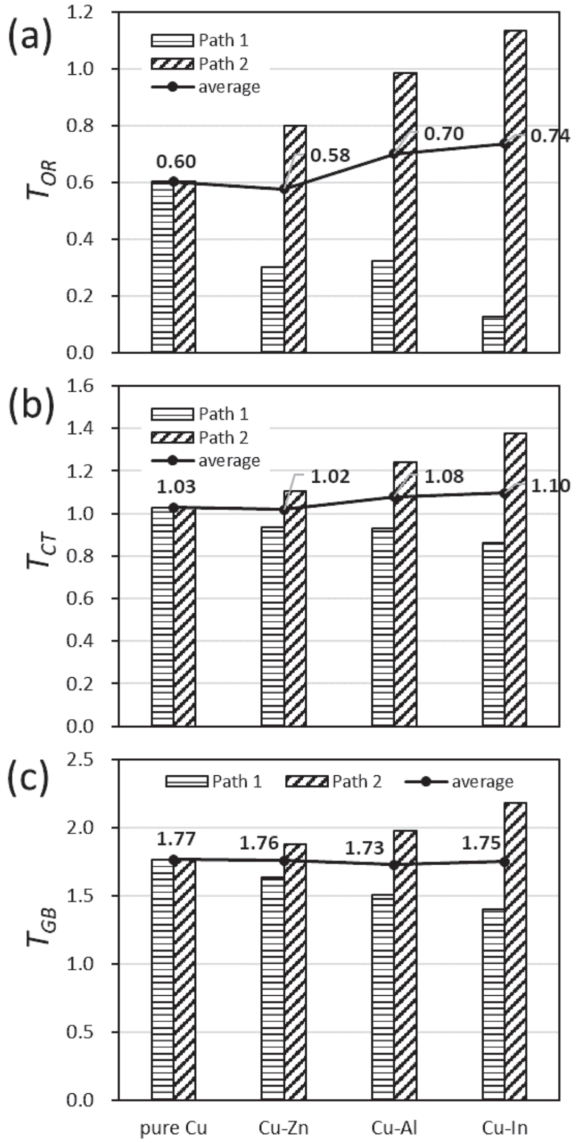

Fig. 6 The calculated twinnability of (a) T_{OR}, (b) T_{CT} and (c) T_{GB} for pure Cu, Cu-Zn, Cu-Al and Cu-In alloys.

indicating that nano-twins can exist very stably once formed. The average α and β are also the smallest in Cu-In alloy among the Cu alloys. It means that by adding indium in copper, we can effectively lower the energy barrier involved in the formation of both the stacking faults and twins. The value of β is highly dependent on the direction when the symmetry is broken as mentioned above, but in practice, there is the random distribution of local strain, lowering the energy barrier for twin formation in all direction.

3.3 The twinnability of Cu-In alloy

The three modes of twinnability for paths 1 and 2 and averaged twinnability (T_{OR}, T_{CT} and T_{GB}) are shown in Fig. 6. In comparison to Al and Zn, In atoms effectively enhances the twinnability of copper. In Cu-In alloy, the T_{OR} and T_{CT} increased by 23% and 7%, respectively, while T_{GB} remained almost unchanged. The increment in T_{OR} and T_{CT} implies that twin formation is activated within the grain and from crack tip rather than the grain boundaries. It is believed that alloying elements capable of inducing significant strain in Cu matrix, similar to In atom, can also play a role in enhancing deformation twinning by breaking the symmetry of copper lattice.

4. Conclusion

We investigated why the deformation twin can easily form in Cu-In alloy based on the density functional theory (DFT) calculations.

(1) To evaluate the twinnability of Cu-In alloy with even distribution of In atoms in Cu matrix, the general stacking fault energies (GSFE), including the unstable stacking fault energy (γ_{usf}), the intrinsic stacking fault energy (γ_{isf}), the unstable twin fault energy (γ_{utf}) and the intrinsic twin fault energy (γ_{itf}), were obtained from DFT simulations and compared to those of pure Cu, Cu-Al alloy and Cu-Zn alloy.

(2) Indium atoms induced lattice strain more than Al and Zn atoms, resulting in severe symmetry breaking. It lowered four stacking fault energies (γ_{usf}, γ_{isf}, γ_{utf}, γ_{itf}) more effectively and the parameter of β ($=\gamma_{utf}/\gamma_{usf}$), which means the energy barrier to generate a twin, can be decreased significantly for a specific <112> slip direction in Cu-In alloy, compared to other Cu alloys.

(3) The averaged twinnability of Cu-In alloy was found to be higher than other Cu alloys. It is anticipated that the random arrangement of slip directions where twins can form easily due to the symmetry breaking will reduce the energy barrier for twin formation throughout the grain in Cu-In alloy.

Acknowledgments

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