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Interactions of point defects with stacking faults in oxygen-free phosphorus-containing copper

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ABSTRACT

The interactions of stacking faults and point defects in oxygen-free phosphorus-containing copper are investigated using *ab initio* methods. Although monovacancies can act as traps for H impurities or OH groups, the calculations show that two vacancies only weakly bind with each other and this interaction terminates at the third nearest-neighbor distance. An interstitial P tends to form a Cu–P dumbbell-like cluster around the lattice site and can readily combine with a vacancy to become a substitutional impurity. It is also found that the intrinsic stacking-fault energy of copper strongly depends on the temperature as well as on the presences of point defects. The intrinsic stacking-fault energy varies between 20 and 77 mJ/m^2 depending on the presence of point defects in the faulted region. These point defects are also found to affect the unstable stacking-fault energy, but they always increase the twinning tendency of copper. Among them, the substitutional P is found to have the strongest effects, decreasing the intrinsic stacking-fault energy and increasing the twinnability.

1. Introduction

Copper is one of the mostly used metals due to its outstanding thermal and electrical conductivity as well as ductility. Oxygen-free phosphorus-containing copper (OFP-Cu) is identified to be the most appropriate canister material for long-term storage of spent nuclear fuel [1]. During the storage, copper will be subjected to both radiation and complex environmental conditions, which may potentially cause the production of point defects and intake of impurities (mostly H and O). To make a reliable prediction of the canister behavior over the long service time, it is important to investigate whether the impurities and point defects that can interact with each other or with extended defects to form defect arrangements that may affect the mechanical properties and thereby cause a loss of the intactness of the canister [2–4].

The OFP-Cu normally contains less than 2 wt. ppm of oxygen and about 50 wt. ppm of phosphorus [1,5]. Oxygen should be eliminated in order to avoid the hydrogen reaction embrittlement [6]. The addition of P improves the creep behavior of oxygen-free copper (OF-Cu) [5,7,8]. Korzhavyi et al. [8] have proposed a mechanism of the P effect on creep ductility, that phosphorus can compete with sulfur for positions in the grain boundary and thus reduces the embrittling effect of the sulfur. However, it was argued that the creep ductility is unrelated to the sulfur content in OF-Cu. Later on, Sandström [5] presented a creep cavitation model that the presence of phosphorus in the grain boundaries of OFP-Cu reduced the amount of grain boundary sliding. This suppressed the nucleation of cavities in the grain boundaries and removed the creep brittleness. However, later research questioned the role of phosphorus in impeding grain boundary sliding. Until now, the exact role of phosphorus in removing the creep brittleness of OF-Cu remains unclear.

Hydrogen uptake by copper canister may happen as a result of the reaction with water [9] (but no final agreement is achieved so far). Hydrogen has only minor effect on the mechanical behavior of nominally pure copper, however, Yagodzinskyy et al. found that hydrogen reduces the tensile strength in slow strain rate tests and enhances the creep rate of copper under continuous electrochemical hydrogen charging [10]. Hydrogen-filled microvoids due to hydrogen-vacancy clustering were found at the creep fracture surface. The detailed mechanism of hydrogen effects on deformation process is unkown. Ganchenkova et al. explicitely studied the interaction between hydrogen and vacancies in copper using numerical simulations [11]. It was found that hydrogen impurities repel one another in the Cu lattice and that the binding of a divacancy is very weak at room temperature. Hydrogen is found to stabilize divacancies and promote further vacancy clustering.

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However, there is very little information on the interactions of point defects with planar defects such as stacking faults (SF). This information is valuable as it is directly related to the deformation behavior of copper.

Twinning and dislocation gliding are the two main competing modes of plastic deformation in face-centered cubic (fcc) metals. The operative mode of plastic deformation is determined by loading conditions and intrinsic properties of materials. The stacking fault energy (SFE) is one of the most important parameters governing the twinnability of fcc metals. Copper has a low SFE value, which is known to be sensitive to alloying [12]. A recent study also shows a strong dependence of the SFE of copper on strain [13], echoing the influences of loading conditions on the deformation behaviors of fcc metals. However, the knowledge on the influences of point defects on the SFE of copper is limited because of the lack of suitable experimental techniques.

In this paper, using *ab initio* methods, we conduct comprehensive studies on point defects in OFP-Cu, the SFE and its variation with temperature and point defect segregation. The interaction of point defects with SF, and the subsequent change of twinnability, are also discussed.

2. Methodology

2.1. Supercell model of SF

The SFE, γ, can be obtained via supercell approach by calculating the free energy difference of supercells having an ideal lattice and a faulted lattice,

$$\gamma = (F_{sf} - F_{id})/A, \tag{1}$$

where F_{sf} and F_{id} are the free energies of supercells with and without stacking faults, A is the stacking fault area. The supercells should be large enough to get an energy convergence. For fcc copper, the ideal stacking sequence along $\langle 1\,1\,1\rangle$ direction should be "...ABCABCABC...". If this order is broken by extracting one plane, *e.g.* plane C between B and A, an intrinsic stacking fault (ISF) is created. If one plane is inserted, *e.g.* plane A between B and C, one gets an extrinsic stacking fault (ESF). The ISF energy (ISFE) and ESF energy (ESFE) are about the same in most cases [14].

The primary slip system corresponding to the lowest-barrier pathway in fcc copper is $\{1\,1\,1\}\langle 1\,1\,2\rangle$ [14]. The generalized stacking fault (GSF) energy (GSFE) can also be calculated using the supercell approach, by sliding the two halves of the supercell with respect to each other along the $[2\,1\,1]_{fcc}$ direction in the $(1\,1\,1)_{fcc}$ plane that is chosen to be the basal plane of the supercell. The Burgers vector changes from [000] to $\frac{1}{6}[=\bar{2}\,1\,1]$, and the maximum of GSFE along the pathway is called the unstable stacking fault energy (γ_{usf}).

2.2. Axial Ising model of SF

The ISFE can also be calculated within the axial Ising model (AIM). The crystal is viewed as a sequence of (1 1 1) planes along the [1 1 1] direction, and only pairwise interaction is assumed in AIM. The corresponding Hamiltonian is

$$H = \sum_{i;n=1,N} J_n \sigma_i \sigma_{i+n} \tag{2}$$

where J_n is the interaction parameter between two planes i and $i+n$. σ_i is a pesudo-spin variable assigned to ith plane depending on whether the stacking sequence of planes i and $i+1$ is correct ($\sigma_i = 1$) or not ($\sigma_i = -1$). Relative to the perfect fcc stacking, the ISFE is expressed as [15,16]

$$\gamma_{isf} = 4(J_1 + J_2 + J_3 + J_4 + \cdots)/A. \tag{3}$$

The ESFE and twin boundary energy are similarly obtained:

$$\gamma_{esf} = 4(J_1 + 2J_2 + 2J_3 + 2J_4 + \cdots)/A, \tag{4}$$

$$\gamma_{twin} = 2(J_1 + 2J_2 + 3J_3 + 4J_4 + \cdots)/A. \tag{5}$$

If the dominant interactions in the system are up to the next-nearest-neighbor plane ($n \leqslant 2$), so that high-order interactions can safely be neglected, the total energies of different stacking sequences will be expressed through J_1 and J_2. With a little bit of algebra, the ISFE, the ESFE and the twin boundary energy can be expressed as:

$$\gamma_{isf} = 4(J_1 + J_2)/A = (F_{hcp} + 2F_{dhcp} - 3F_{fcc})/A, \tag{6}$$

$$\gamma_{esf} = 4(J_1 + 2J_2)/A = 4(F_{dhcp} - F_{fcc})/A, \tag{7}$$

$$\gamma_{twin} = 2(J_1 + 2J_2)/A = 2(F_{dhcp} - F_{fcc})/A. \tag{8}$$

This is called axial next-nearest-neighbor Ising (ANNNI) model. The F_{hcp}, F_{dhcp} and F_{fcc} are the free energies of the fcc, hcp (hexagonal close-packed), and dhcp (double hexagonal close-packed) structures. The ISFE and ESFE of copper are obtained to be nearly the same from the ANNNI model in our calculations, and the twin energy is half of the ESFE. So, in this work, we only focus on the ISFE of copper.

2.3. Free energy calculations

The structure relaxations and total energy calculations were performed using the Vienna *ab initio* simulation package (VASP) based on the density functional theory (DFT) [17,18], applying the projector augmented wave (PAW) potentials [19–21]. Cu-$3d^{10}4s^1$, O-$2s^22p^4$, H-$1s^1$ and P-$3s^23p^3$ were treated as valence electrons. Exchange–correlation was treated by local density approximation (LDA), and generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) scheme [22] and PBEsol scheme [23].

Critical energy convergency was checked with respect to the plane-wave cut-off energy and k-mesh. With a cut-off energy of 550 eV and a k-mesh of $22 \times 22 \times 22$ using Monkhorst–Pack scheme, the total energy of the fcc unit cell of copper was converged within 1 meV. The same cut-off energy and equivalent k-mesh were then used for all the following calculations. A test of the three exchange–correlation density functionals have been done in comparison with experimental data. The results are shown in Table 1. PBE gives better description than LDA, as also found by Ganchenkova et al. [11]. The calculated values by PBEsol functional are always in between those of PBE and LDA. Since the differences between the results of PBE and PBEsol are not evident and we have more PBE data from previous calculations, PBE functional was used for the calculations in this work (unless stated otherwise).

Table 1
Computed lattice parameter (in Å), monovacancy formation energy E_f(V), binding energy of a monovacancy to one H in octahedral site E_b(VH) (in eV), and the intrinsic stacking-fault energy (in mJ/m^2), in comparison with experimental data.

	a	E_f(V)	E_b(VH)	γ_{isf} (mJ/m^2)	
	Å	eV	eV	ANNNI	Supercell
PBE	3.635	1.06	−0.25	41	40
PBEsol	3.569	1.24	−0.27	45	–
LDA	3.524	1.26	−0.28	51	–
Exp.	3.615[a]	0.92–1.31[b]	−0.4[c]	30–80[d]	

[a] Ref.[27].
[b] Refs.[28,29].
[c] Refs.[30–32].
[d] Ref.[12]