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Investigation of impurity induced twinning in MgO from first principles calculations

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ABSTRACT

In this work, we investigated using first principles calculations the effects of impurity atoms (Ca and Ti) on the deformation mechanisms, the formations of deformation twin and growth twin in MgO. We found that the deformation mechanism may be changed from perfect dislocation glide to twinning by introducing the impurities. Further studies showed that deformation twins may appear in the Ca impurity systems, where the preferred slip system may be changed from $\{1\,1\,0\}\langle 1\,1\,0\rangle$ to $\{1\,1\,1\}\langle 1\,1\,2\rangle$. In contrast, growth twin may become the major mode of the twin formation in the Ti impurity systems due to the negative generalized stacking fault energy and twin boundary energy along $\{1\,1\,1\}\langle 1\,1\,2\rangle$ slip system. Moreover, the chemical bonds near the impurity atoms have a tendency of being covalent.

1. Introduction

Magnesium oxide (MgO) has a broad range of technological applications, such as insulators, heat resistors, substrates, barriers in tunneling magneto resistive devices, etc. [1,2]. Researches showed that it is perhaps one of the best characterized oxide materials in terms of grain boundaries (GBs) and defects [3–6]. It is known that the combination of structural defects with crystalline lattices may play an important role in the mechanical properties of the material. It has been shown in many researches that twin boundaries (TBs), which are more energetically stable than the conventional GBs, may exhibit much stronger strengthening effect than the latter [7–11], implying a promising way to enhance the strength of a material without losing ductility by introducing TBs into a material [12]. However, it is difficult for twins to form in most ceramic materials during deformation, taking MgO as an example, where the formation of growth- or deformation-twins are almost impossible because of its high twin boundary energy (TBE) [13].

Doping impurities into ceramics is a common and effective method to induce twins and usually adopted in practice [14,15]. Doping impurities into bulk materials can help the formation of stacking faults, which is a prerequisite for the formation of deformation twins [16,17]. Impurity atoms can induce the twins in B1 structured TiC due to the negative TBE [18], which has been confirmed by experiments [16,17]. Akchurin et al. reported that deformation twinning is the main mechanism of the plastic deformation in a MgO + AlO_3 system [19]. Wang et al. [3,20] found that Ca and Ti impurities can congregate to the GBs in MgO, forming a periodic mixed interface. They further demonstrated by experimental observations and theoretical calculations that Ca impurity is segregated to the boundary structural units, which may induce structural transformation; and Ti atoms prefer to exist as substitutional ones in MgO [5,21]. Sun et al. [22] found that Cr doping can drastically decrease the elastic moduli of $MoSi_2$, while Nb doping can significantly increase the ratio of bulk modulus (B) to shear modulus (G) and the Poisson's ratio, contributing to good ductility and strong metallic bonding. Du et al. [23] reported that the hardness, density, wear resistance and thermal expansion coefficient of SiC can be improved by Si impurities.

Generalized stacking fault energy (GSFE), which can be determined from a relative shear displacement between two adjacent atomic planes by a prescribed slip system, can be used to evaluate the resistance to the nucleation and glide of dislocations [24–26]. Although many researches have been made on the effects of impurity atoms on the grain boundary structure, some problems still remain unclear, for example, the effects of impurity atoms (Ca or Ti) on the GSFEs of MgO, especially, whether these impurity atoms can help the formation of twin structures in MgO.

In this work, we will investigate the effects of the impurities of Ca and Ti on the deformation and formability of twinning in MgO, using first principles calculations, and gain an insight into the mechanisms for the formation of twin structures in MgO.

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Table 1
Comparison of our calculated results with others' experimental and calculated results.

	Our results	Others' Cal. results [34,35]	Exp. results [13,32–36]
Lattice parameter (Å)	4.237	4.237–4.25	4.21–4.22
Bulk modulus (GPa)	160	163	162
C_{11} (GPa)	267	169–279	297
C_{12} (GPa)	92	93–95	95
C_{44} (GPa)	145	146	156

2. Calculation details

The Vienna Ab-initio Simulation Package (VASP), which is based on density function theory (DFT), is used in our calculations [27,28]. The projector augmented wave (PAW) method is employed for the evaluation of electron-ion interactions [29,30] and the generalized gradient approximation (GGA) by Perdew-Buke-Ernzerhof (PBE) of exchange functional is adopted to describe the exchange-correlation functional in all calculations [31]. The single particle Kohn-Sham wave functions are expanded using plane waves with a cutoff energy of 450 eV. Samples of irreducible Brillouin-zone are implemented in the regular Monkhorst-Pack (MP) grid with 11 × 11 × 11 *k*-points and 5 × 5 × 1 for bulk and surface calculations, respectively. During the relaxation, the convergence criteria of the total energy and force on each atom are set as 10^{-5} eV and 0.03 eV/Å, respectively. Table 1 shows the lattice parameters, bulk modulus and elastic constants of rock-salt crystal structured MgO obtained in our calculations, which are in good agreement with the experimental and calculated results by other researchers.

The concept of GSFE was proposed by Vitek [24]. It considered a perfect crystal cut into two identical parts with a single plane, which are subjected to a relative displacement $\boldsymbol{d}$ and then rejoined, and the rejoined lattice had a surplus energy per unit area defined as

$$\gamma_d = \frac{E_d - E_0}{A} \tag{1}$$

where E_0 and $E_{\boldsymbol{d}}$ are the potential energies of the system before and after the application of $\boldsymbol{d}$, and A is the stacking fault area. The GSFE curve has been widely used to analyze the deformation mechanisms of materials [35,37,38].

In our calculation of GSFE, a vacuum layer of 15 Å in thickness is established, which serves as a buffer zone to avoid the disturbance between the adjacent slabs [18], as shown in Fig. 1(a), where *x*-, *y*- and *z*-directions correspond to [1 1 $\bar{2}$], [$\bar{1}$ 1 0] and [1 1 1], respectively, and periodic conditions are applied in all the three directions. In the GSF calculations, the atoms at the top and the bottom of the slab are not allowed far away from the interface to mimic bulk like behavior. We have two possible ways to imitate the bulk-like behavior. In the first one, the model is sufficiently thick so that rigid shear would not affect the atoms at the top and the bottom of the model. In the other one, the atoms at the top and the bottom of the model are fixed directly. Suppose periodic boundary conditions have been applied in both *x*- and *y*-directions, we will test the effects of the two kinds of boundary conditions, i.e., with the top and the bottom atoms fixed and unfixed in z-direction, respectively (see Fig. 1(a)), during the calculation of GSFE. Fig. 1(b) and (c) show the calculated GSFE curves of {1 1 1}⟨1 1 0⟩ and {1 1 1}⟨1 1 2⟩ slip systems in the samples of thickness containing respectively 19, 55 and 67 layers of atoms, with the upper surface atoms fixed and unfixed in z-direction, respectively. It can be seen in Fig. 1(b) and (c) that the GSFE curves of the samples containing respectively 55 and 67 layers, with and without fixing the top and bottom atoms in z-direction respectively, coincide well with each other, with the maximum error less than 2.5%, which are also consistent well with the results by others [32,39,40]. Considering both accuracy and calculation efficiency, we choose the samples of thickness containing 55 layers of atoms with the upper surface atoms unfixed in the following calculations.

3. Results and discussion

3.1. Effects of Ca or Ti doping on GSFE curves

To investigate the effects of Ca or Ti doping atoms, the models containing substitutional Ca or Ti atoms are built for the calculations of GSFE curves. The models involve two cases: (1) a Mg atom in the plane L0 is replaced with a Ca or Ti atom, where L0 also serves as the glide plane; (2) the corresponding models consists of pure MgO, without any atoms being substituted with impurity atoms. Fig. 2(a)–(c) show the models with substitutional impurity atoms and possible slip directions on {0 0 1}, {1 1 0} and {1 1 1} planes, respectively.

MgO is of B1 lattice structure. Since the shortest Burgers vector for possible perfect dislocations is $a_0/2$ ⟨1 1 0⟩ in B1 structure, where a_0 is the lattice constant [27], the GSFE curves along the ⟨1 1 0⟩ direction on the {0 0 1}, {1 1 0} and {1 1 1} planes are calculated and shown in Fig. 3. It was reported that {1 1 1}⟨1 1 2⟩ Shockley partial dislocations are the prerequisite for the formation of deformation twin in B1 structure of VN [26], therefore, the GSFE curves along {1 1 1}⟨1 1 2⟩ slip systems are also calculated and shown in Fig. 3.

We first calculate the GSFE curves of pure MgO along the four candidate slip systems, and the results are shown in Fig. 3(a). These curves are symmetrical except that of {1 1 1}⟨1 1 2⟩ slip system, where there is a platform followed by a sharp ascent to the peak. The platform corresponds to the stable stacking fault energy (γ_{is}) related to the slip of Shockley partial dislocations. The energy barriers of these curves are 2.05 J/m^2 for {0 0 1}⟨1 1 0⟩ slip system (abbreviated to Max. V of {0 0 1}⟨1 1 0⟩), 0.97 J/m^2 (Max. V of {1 1 0}⟨1 1 0⟩), 2.35 J/m^2 (Max. V of {1 1 1}⟨1 1 0⟩) and 1.55 J/m^2 (the value at the lower platform of {1 1 1}⟨1 1 2⟩), among which the lowest energy barrier is 0.97 J/m^2 of {1 1 0}⟨1 1 0⟩ slip system, implying that the most preferred slip system should be {1 1 0}⟨1 1 0⟩, where the nucleation and glide of perfect dislocation should be the main deformation mechanism, which is in agreement with that in the previous studies [32,39]. The energy barrier for the slip of Shockley partial dislocations along {1 1 1}⟨1 1 2⟩ slip system is about 1.6 times that for the slip of dislocation along {1 1 0}⟨1 1 0⟩ slip system, indicating the activation of Shockley partial dislocations should be more difficult.

Fig. 3(b) shows the GSFE curves of MgO doped with Ca along the four candidate slip systems. It can be seen that the shapes of these curves are similar to that of pure MgO, but the energy barriers of the curves of {1 1 1}⟨1 1 2⟩ and {0 0 1}⟨1 1 0⟩ descend markedly. The comparison between the energy barriers of the four slip systems shows that the barrier of {1 1 1}⟨1 1 2⟩ slip system is the lowest, indicating that the glide along {1 1 1}⟨1 1 2⟩ should be the easiest, therefore, the nucleation and glide of Shockley partial dislocations should dominate the initial inelastic deformation. It is known that the sequential activation and glide of Shockley partial dislocations may result in the formation of deformation twin, indicating that deformation twinning will dominate the inelastic initial plastic deformation in MgO doped with Ca. It should be noted that the energy barrier along {1 1 0}⟨1 1 0⟩ is slightly higher than that along {1 1 1}⟨1 1 2⟩, therefore, the nucleation and glide of {1 1 0}⟨1 1 0⟩ dislocations should serve as another possible mechanism of initial plastic deformation, which would work once the glide along {1 1 1}⟨1 1 2⟩ is hindered due to the increase in the GSFE with respect to the slip distance, as can be seen in Fig. 3(b).

Fig. 3(c) shows the GSFE curves of MgO doped with Ti of the four candidate slip systems, where the energy barrier of each slip system decreases obviously compared with its counterpart of pure MgO (Fig. 3(a)). The lowest energy barrier among the GSFE curves still lies in that of {1 1 0}⟨1 1 0⟩ slip system, therefore, the nucleation and glide of perfect dislocations should dominate initial plastic deformation, which