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Ab initio study of the likely orientation relationships of interphase and homophase interfaces in a two-phase HCP + BCC Mg-Li alloy

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ABSTRACT

Density functional theory is employed to examine the properties of interfaces generated between the hexagonal close packed (HCP) α and body centred cubic (BCC) β phases in a Mg-8wt.%Li binary alloy. While there are four experimentally-observed and geometrically-predicted orientation relationships (OR) associated with these adjoining HCP and BCC structures, interfacial energy considerations govern the most likely choice of OR. Here, the Burgers OR was found to have the lowest interfacial energy and the largest work of separation. It was also shown that homophase β/β interfacial energies are much higher than the interfacial energy of the α/β phases exhibiting the Burgers OR as the preferred OR. The findings are consistent with the hypothesis that the energy of a preferred interface corresponds to a local minimum in the five-dimensional boundary geometrical phase space. In addition, it was revealed that occupied s bands of the local electronic density of states of atomic layers in the vicinity of the α/β interface exhibiting the Burgers OR shift towards lower electronic energies, thereby increasing the interface stability. The crystal orbital Hamiltonian population provided further quantitative evidence that such an interphase interface of Burgers OR represents the strongest covalent bonding, thereby indicating that chemical bonding constitutes an essential contribution to the interfacial energy. Hence, the simple association between geometrical parameters of an interface and interfacial energy is incomplete.

1. Introduction

It is well-established that in the nucleation and growth of a new α phase of crystal structure A in the β matrix of crystal structure B, the driving force for the transformation is counterbalanced by an energy barrier comprising both the energetic cost of creating the α/β interface and the associated strain energy [1]. Contrary to non-diffusional displacive phase transformations where the reduction in strain energy associated with the transformed region dominates the crystallographic feature of the transformation (i.e. the orientation relationship between parent and product phases and the morphology of the latter), in reconstructive diffusional phase transformations, the interfacial energy is believed to play a dominant role [1,2]. At equilibrium, the energy barrier to diffusional phase transformation is minimized and the preferred interfacial crystallographic characteristics correspond to a local minimum in the five-dimensional boundary geometric phase space comprising two macroscopic degrees of freedom along the rotation axis, one for the rotation angle and the last two associated to the normal to the interface plane [3]. Indeed, the all-important interfacial energy is the fundamental parameter determining the stable interface configuration [4].

In addition, dual-phase alloys are becoming increasingly important as structural materials [5–9] and Mg-Li binary alloys can serve as a good example here since the crystal structure of this alloy system is hexagonal close packed (HCP) α and body centred cubic (BCC) β for Li contents less than ~5 wt% and greater than ~10 wt %, respectively, separated by the α + β phase field containing a eutectic reaction at ~8 wt% Li [6]. Moreover, Mg-Li-based alloys have attracted considerable interest since their initial development in 1960s as potential ultra-lightweight structural materials with improved ductility. In addition to their use as structural alloys, they also have potential applications in batteries due to their electrochemical properties [6,10,11]. Most recently, a low density Mg-Li-based alloy was developed with a formidable property profile of high strength, good ductility and excellent corrosion resistance [6].

Nie and co-workers [12] studied the crystallographic nature of the BCC/HCP interface created during the precipitation of α within the supersaturated β matrix of a Mg-8 wt% Li alloy using transmission electron microscopy (TEM). Selected area diffraction (SAED) revealed that the α/β interface is coherent, consisting of parallel

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close packed planes $(0001)_\alpha$ and $(0\bar{1}1)_\beta$ together with parallel close packed directions $[11\bar{2}0]_\alpha$ and $[111]_\beta$ [12]. The habit plane was found to be $(1\bar{1}00)_\alpha/(\bar{2}11)_\beta$. Such crystallographic characteristics of the HCP α/BCC β interface in this Mg-Li alloy is consistent with the Burgers orientation relationship (OR) [13]:

$$\text{Burgers}: (0001)_\alpha||(0\bar{1}1)_\beta, [11\bar{2}0]_\alpha||[111]_\beta$$

It is worth noting that subsequent experimental observations have identified three other main HCP/BCC ORs [14]:

Pitsch-Schrader (P-S): $(0001)_\alpha||(0\bar{1}1)_\beta$, $[11\bar{2}0]_\alpha||[100]_\beta$;
Potter: $(0001)_\alpha$ 2° from $(011)_\beta$, $(01\bar{1}1)_\alpha||(110)_\beta$, $[2\bar{1}\bar{1}0]_\alpha||[1\bar{1}1]_\beta$, and
Rong-Dunlop (R-D): $(0001)_\alpha||(021)_\beta$, $(1\bar{1}00)_\alpha||(0\bar{1}2)_\beta$, $[2\bar{1}\bar{1}0]_\alpha||[100]_\beta$.

Various geometrical models, including invariant line, structural ledge, O-lattice and edge-to-edge matching models [2,15], have been developed over the years for predicting the myriad experimentally-observed ORs generated between a product and parent phase by a diffusional transformation. The invariant line model assumes that a major reduction in the energetic barrier to the nucleation of the new phase can be achieved by the generation of an invariant line in the interface along which atoms are perfectly matched and atom misfit and, hence, strain energy is minimized [2,16]. The structural ledge model presumes that maximizing atom matching is best achieved between parallel close-packed planes of the product and matrix phases [17]. The premise of the O-lattice approach is that atomic matching across an interface is determined by the proportion of coincidence or near coincidence sites relative to the product and matrix crystal structures [2]. Finally, the edge-to-edge matching model underlines the significance of atom row matching to minimize interphase interfacial energies [2,18].

These foregoing models and in particular the edge-to-edge matching method have been successful in predicting numerous experimentally-observed ORs, including the Burgers OR in the Mg-8wt.%Li α + β alloy [19,20]. However, the models are purely geometrical [2,15] and provide limited insight into the interfacial properties of the adjoining phases. Sutton and Balluffi [21] compared a number of experimental measurements of interfacial energy against purely geometric criteria such as low Σ sites (i.e. reciprocal volume density of coincident site lattice (CSL)), high planar CSL site density (Γ), high Γ at constant interplanar spacing (d), large d and high density of locked-in rows of atoms. They concluded that the simple geometric framework failed to show any general criteria for low interfacial energy [21].

More recently, a large number of distinct grain boundaries in face centred cubic (FCC) Ni and Al were simulated using interatomic potentials based on the embedded atom method, to examine the correlations between boundary energy and misorientation angle, Σ value, excess boundary volume and the boundary normal proximity to ⟨1 1 1⟩ direction. It was found that the usual geometric properties failed to correlate to lower energies [22]. In fact, the association of geometrical features to interfacial energy remains obscure [15] due to neglecting the physical atomic interactions at a given interface. Such interactions may vary according to the nature of interfacial bonding. For example, it has been observed that, while low energy grain boundaries in ionic crystals correspond to nearest neighbor ions having different signs, in covalent systems grain boundary energy is mostly governed by the saturation of bonds [17]. Besides, in crystalline metals, the coordination number of polyhedra at low energy grain boundaries tend to match the coordination number of the perfect crystal as closely as possible [21]. Moreover, local configurational relaxations in the vicinity of the interfaces may have a significant role in reducing the interfacial energy [4]. Indeed, while there are well-established thermodynamic and kinetic theories for precipitation reactions, the factors determining their crystallographic characteristics are yet to be further explored [15].

It is worth noting that atomistic simulations have played a vital role in computing the energy and structure of single- and dual-phase boundaries [22]. However, unraveling the nature of interfacial bonding based on the local electronic structure of an interface can be fulfilled primarily via ab initio calculations. In this work, we have applied first principles to simulate the α + β interphase interface observed in the Mg-8 wt% Li alloy and computed the energetic cost of creating such an interface for various ORs. In addition, the local density of electronic states in the vicinity of the interface was used for explaining the effect of bonding on the stability of ORs between a parent and product phase.

2. Computational method

First principles calculations based on density functional theory were carried out to find the α/β interfacial properties of a Mg-8wt.%Li binary alloy. Vienna ab initio software package (VASP) was used [23] implementing the projector augmented wave method to represent the combined potential of core electrons and nuclei [24]. The exchange and correlation energies were approximated as a generalized gradient functional [25]. A cut-off energy of 390 eV was chosen for the plane wave basis and the self-consistent electronic optimization was converged to 10^{-7} eV. The supercells containing interfaces were configured in the form of adjacent two slabs of structures A and B, respectively, with a vacuum layer of 10 Å on top. Periodic boundary conditions were applied in three dimensions and the mesh of Γ-centred k-points to sample the Brillouin zone were chosen such that the density of them is less than 0.032 $A°^{-1}$. Tests were performed to ensure that an effective convergence is attained with respect to the thickness of slabs, the vacuum layer and the density of k-points.

Fig. 1(a) depicts schematically the interface between HCP α and BCC β matrix, as described by the Burgers OR: $[0001]_\alpha||[0\bar{1}1]_\beta$, $(\bar{1}100)_\alpha||(\bar{2}11)_\beta$. The lattice parameter of β is set to the reported experimental value of 351.4 pm [12] and the total number of atoms in the supercell is provided in Table 1. While the observed lattice constants of the α HCP phase are 319.4 and 512.6 pm the initial setup of the interphase boundary is assumed to be coherent since accommodating the misfit between the precipitated plates and the parent matrix requires a very large supercell and such calculations are deemed impractical [26]. As such, the lattice parameters of the precipitate plates for the initial configuration of the interface are reduced by 4.7% in the basal plane and 3.0% along the c axis, respectively. The atomic configuration is free to relax in three dimensions such that all atomic forces become less than 0.01 eV/Å [27].

To obtain a comparative assessment of the α/β interfacial properties, slabs representing P-S and R-D ORs were also constructed as shown in Fig. 1(b) and (c), respectively. To avoid impractical large supercells, initial setups of both ORs are also considered to be coherent and the number of atoms in the supercell is listed in Table 1. As a consequence, the change in the α phase lattice parameters are 3.7% and −3.0% for the former and −1.6% and 2.2% for the latter ORs, respectively. It is pertinent to note that the Potter interface was not simulated because, in the coherent approximation, it is quite similar to the Burgers OR.

The work of separation (W_{sep}), defined as the reversible work needed to separate the interface into two free surfaces, the free surface energy (σ) and interfacial energy ($\gamma_{\alpha||\beta}$), respectively, are expressed as [28,29]: