Grain-Boundary Diffusion by Vacancy Mechanism in $\alpha$-Ti and $\alpha$-Zr

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Minimum-energy structures for the symmetric ($1\bar{1}2\bar{1}$) and ($1\bar{1}2\bar{2}$) twin grain boundaries (GBs), as well as for two nonsymmetric GBs that exhibit dislocations, are obtained for the hcp structure by computer modeling. Central force potentials constructed within the embedded-atom method are used to represent atomic interactions. Vacancy-formation energies and entropies for different sites are calculated, and the properties of various vacancy jumps are investigated. Unstable vacancy sites, located in the GB dislocation cores, are observed. The random-walk approach, combined with simulation results, is applied to study tracer diffusion by a vacancy mechanism in the twin GBs; higher diffusivity values than those for the lattice are obtained, in qualitative agreement with experiments. Correlation effects, taken into account by the matrix method, determine the main features of GB diffusion to be contributed by jumps in a narrow region.

I. INTRODUCTION

The great difference between the atomic structure of grain boundaries (GBs) and of the bulk determines significant differences in their physical properties. Regarding point-defect properties, the low formation and migration energies found by computer simulation studies in the GB region help to provide an explanation for the fast diffusion experimentally observed in many polycrystalline metallic systems. Although strong correlation effects associated with the nonuniformity of the GB structure, as well as with the type of point defect involved in the mass-transport process, may exist, diffusion can be several orders of magnitude higher than in the bulk. This character of short-circuits for diffusion gives the GB a key role in several metallurgical processes that take place at usual working temperatures, such as creep, corrosion, solid-state transformations, etc. Also, the possible accumulation of point defects at those regions, another consequence of the aforementioned low formation energies, may degrade the material mechanical properties, having then an evident impact on its macroscopic behavior.

Regarding computer simulation studies of GB structures and their interaction with point defects, the literature on the hcp lattice is rather scarce, in spite of the relevance that materials such as Zr and Ti have to different industries. Early works have employed pair interatomic potentials. More recent works incorporate many-body potentials. In Reference 6, the formation and migration of vacancies in the minimum-energy structure for the ($1\bar{1}2\bar{1}$) twin GB have been analyzed in $\alpha$-Zr and $\alpha$-Ti. The energies, entropies, and relaxation volumes associated with different vacancy locations and vacancy jumps have been calculated. Then, boundary diffusion has been evaluated on the basis of the most probable paths proposed from the simple jumps, considering correlations within a rough approximation. That study is completed in the present work by explicitly calculating partial correlation factors using the well-known matrix method. Also, the minimum-energy structure, defect properties, and diffusion are analyzed for the ($1\bar{1}2\bar{2}$) twin GB in $\alpha$-Zr and $\alpha$-Ti, as well as the minimum-energy structure for two nonsymmetric GBs in Zr and the vacancy properties for only one of them.

The article is organized as follows: the calculation procedure employed to determine minimum-energy structures is described in Section II; the results obtained regarding the GB structure and some vacancy properties for symmetric and nonsymmetric GBs are summarized in Section III; a brief description of the random-walk approach and the matrix method employed to evaluate correlation effects are the subject of Section IV, including the diffusion results; and finally, the relevant findings are summarized in Section V.

II. CALCULATION PROCEDURE

The procedure followed to determine the GB structures of lowest energy consists of (1) construction of a bicrystal with a given geometrical boundary and (2) minimization of the system energy by relaxing the atomic configuration. To accomplish step 1, two interpenetrated coincident crystals are rotated, one with respect to the other, about the [1100] direction until coincidence of two vectors, $\mathbf{u} = n\mathbf{e}_1 + m\mathbf{e}_2$ for one grain and $\mathbf{v} = k\mathbf{e}_1 + l\mathbf{e}_2$ for the other, is obtained. Here, $\mathbf{e}_1 = a/3[11\bar{2}0], \mathbf{e}_2 = c[0001],$ and $m, n, l, k$ are integers. Nontrivial solutions can only be obtained if $(c/a)^2$ is rational. By choosing $(c/a)^2 = 33/13$, which differs by less than 0.1 pct from the experimental value, relatively short periods on the GB may be obtained. To accomplish step 2, periodic boundary conditions are applied in two directions parallel to the boundary plane. In the perpendicular direction, both grains are ended by slabs of fixed atoms at perfect lattice positions. Rigid relative translations of the...
grains parallel to the GB plane are then applied, searching for a minimum in the energy. Then, the energy is minimized by individual atom relaxations and slab rigid translations, according to the conjugate gradient method. This assures the condition of zero stress normal to the slabs and relaxed forces, acting on any of the atoms, lower than $10^{-5}$ eV Å$^{-1}$. Sometimes it was found to be more efficient to replace the rigid slabs by free surfaces, particularly for the nonsymmetric GBs. In practice, the free atoms remain in perfect lattice positions at distances greater than about five basal lattice parameters away from the boundary on either side.

The symmetric GBs studied in the present work are the ones characterized by the twinning plane $K_1 = (1121)$, twinning direction $\eta_1 = [T \, \bar{T} \, 2 \bar{6}]$, conjugate plane $K_2 = (0001)$, and conjugate direction $\eta_2 = [1 \bar{1} \bar{2} \bar{0}]$ and the one characterized by $K_3 = (1 \bar{1} \bar{2} \bar{2}), \eta_3 = [1 \bar{1} \bar{2} \bar{3}], K_4 = (1 \bar{1} \bar{2} \bar{4})$, and $\eta_2 \equiv [2 \bar{2} \bar{4} \bar{3}]$. While the relaxed structure for the first GB is invariant with respect to a 180 deg rotation about the $\eta_1$ axis, the second has reflection symmetry with respect to $K_1$. These structures are schematically depicted in Figure 1.

A nonsymmetric GB is characterized by a plane and two directions on each grain of the bicrystal. One of these directions being the tilt axis [1100], the GB hereafter called NS1 is described by $(\bar{7} \, \bar{7} \, 14 \, \bar{8}) [4 \, 4 \, \bar{8} \, 2 \bar{1}]$ and $(\bar{3} \, \bar{3} \, 6 \, 7) [7 \, 7 \, 14 \, 18]$, and the one called NS2 is described by $(\bar{7} \, \bar{7} \, 14 \, \bar{8}) [4 \, 4 \, \bar{8} \, \bar{2} \bar{1}]$ and $(\bar{3} \, \bar{3} \, 6 \, 7) [7 \, 7 \, 14 \, 18]$. The relaxed configurations for both GBs are shown in Figure 2.

The equilibrium interatomic potentials used in this work for the symmetric GBs in $\alpha$-Ti and $\alpha$-Zr have been constructed in the past and are indicated as Ti1 and Zr in Reference 6. Regarding the nonsymmetric structures, we have refitted the potentials to the aforementioned $c/a$ ratio in order to avoid spurious stresses. The new versions reproduce practically the same values for the lattice vacancy-formation energy and entropy.

To calculate the vacancy properties in the GBs, a spherical cluster centered at the defect and intersected by the GB was used. Constant-volume boundary conditions were applied to these simulations; a cluster of 1000 atoms was sufficient to obtain well-converged energy and entropy values.

III. RESULTS ON GB STRUCTURE AND VACANCY PROPERTIES

A. Lowest-Energy Structures

In the present work, and according to the structural multiplicity previously found in atomistic studies of GBs, several relaxed configurations are obtained from given bicrystal orientations. For each potential used, the configurations correspond to different relative displacements of the grains and have different energies. However, symmetric configurations with different initial geometric setups result, after relaxation,