Acta Materialia 103 (2016) 573–586

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Diffusion coefficients of alloying elements in dilute Mg alloys: A comprehensive first-principles study

Bi-Cheng Zhou*, Shun-Li Shang, Yi Wang, Zi-Kui Liu

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 24 May 2015
Received in revised form
23 September 2015
Accepted 6 October 2015
Available online xxx

Keywords:
Magnesium alloys
Bulk diffusion
First-principles calculation
Kinetics

ABSTRACT

First-principles calculations based on density functional theory have been used to calculate the temperature-dependent dilute tracer diffusion coefficients for 47 substitutional alloying elements in hexagonal closed packed (hcp) Mg by combining transition state theory and an 8-frequency model. The minimum energy pathways and the saddle point configurations during solute migration are calculated with the climbing image nudged elastic band method. Vibrational properties are obtained using the quasi-harmonic Debye model with inputs from first-principles calculations. An improved generalized gradient approximation of PBEsol is used in the present first-principles calculations, which is able to well describe both vacancy formation energies and vibrational properties. It is found that the solute diffusion coefficients in hcp Mg are roughly inversely proportional to the bulk modulus of the dilute alloys, which reflects the solutes' bonding to Mg. Transition metal elements with *d* electrons show strong interactions with Mg and have large diffusion activation energies. Correlation effects are not negligible for solutes Ca, Na, Sr, Se, Te, and Y, in which the direct solute migration barriers are much smaller than the solvent (Mg) migration barriers. Calculated diffusion coefficients are in remarkable agreement with available experimental data in the literature.

1. Introduction

In recent years, magnesium (Mg) alloys have received an increasing interest due to their low density, earth abundance, high specific strength, and good castability [1]. These properties make Mg alloys attractive for automotive, aerospace, and other lightweight structural applications [2]. The majority of Mg alloys derives their mechanical properties from precipitation hardening [3], while the study of precipitation process demands accurate thermodynamic and kinetic (diffusion) data. Thermodynamics of Mg alloys has been extensively studied, and several comprehensive thermodynamic databases have been established [4]. However, the kinetics of Mg alloys has been studied to a far lesser extent, especially diffusion coefficients of various solutes in Mg. Due to the issues related to corrosion, surface oxidation, and contamination of impurities during sample preparation in diffusion measurements, few experimental data are available in the literature for diffusion coefficients of solutes in Mg [5].

For the investigation of kinetic processes in Mg alloys in the solid state, such as creep [6], solute strengthening [7,8], solution treatment and aging [9], reliable diffusion data and detailed insights into diffusion of solutes in Mg are desperately needed. For example, the knowledge of diffusion coefficients can help to determine the desirable aging time to achieve peak hardness in precipitation-hardened Mg alloys [3]. Wrought Mg alloys have seen very little implementation in the automotive industry because of their poor formability at room temperature [6]. To improve the formability of wrought Mg alloys, proper alloying additions can be selected by evaluating their solute drag propensity at the grain boundaries [10] to mitigate the basal plane texture formation due to the anisotropic deformation of hcp Mg. This propensity greatly depends on their diffusion coefficients based on Cahn's solute drag theory [11]. Diffusion of solutes around the dislocation core structure in Mg also plays an important role in understanding the origin of many plastic phenomena such as dynamic strain aging [7] and plastic instabilities [12]. Therefore, the information of solute diffusion coefficients in Mg is critical for the development of new casting and wrought Mg alloys.

Fortunately, it is now possible to calculate many aspects of diffusion [13,14]. First-principles calculations based on density

* Corresponding author.
E-mail addresses: zhoubicheng@gmail.com, bicheng.zhou@psu.edu (B.-C. Zhou).

http://dx.doi.org/10.1016/j.actamat.2015.10.010
1359-6454/

functional theory (DFT) have been extensively used to calculate diffusion coefficients, especially when experimental data are lacking [15,16]. These calculations are usually coupled with transition state theory (TST) under the harmonic or the quasi-harmonic approximations [14]. TST has become a practical tool in the context of DFT calculations when efficient algorithms for finding the minimum-energy path have been developed, such as the nudged elastic band (NEB) and the climb image nudged elastic band (CI-NEB) method [17]. At present, first-principles calculations of diffusion coefficients are largely limited to cubic systems, such as those in Al [15,18], Fe [19,20], and Ni [21–23] alloys. This is due to the additional complexity of anisotropy associated with the calculations of diffusion coefficients in hcp systems. Recently, Ganeshan et al. [16] in our group calculated the diffusion coefficients of Al, Zn, Sn, and Ca in dilute hcp Mg using an 8-frequency model. However, their calculated results compared with experimental data still need to be further improved (see details in Section 4), and especially more alloying elements need to be considered for Mg alloys.

In the present study, we use first-principles calculations coupled with the TST and the 8-frequency model to calculate the dilute solute tracer diffusion coefficients in hcp Mg. Forty-seven substitutional alloying elements have been considered herein, namely Ag, Al, As, Au, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, Ir, Li, Mn, Mo, Na, Nb, Ni, Os, Pb, Pd, Pt, Re, Rh, Ru, Sb, Sc, Se, Si, Sn, Sr, Ta, Tc, Te, Ti, Tl, V, W, Y, Zn, and Zr (see also Fig. 1). The self-diffusion coefficients of Mg have been calculated as well. The effects of different exchange–correlation (X–C) functionals on diffusion properties are examined. It is shown that the recently developed PBEsol X–C functional [24] yields better agreement with experimental data compared with the commonly used X–C functionals such as the local density approximation (LDA) and the generalized gradient approximation (GGA) for the self-diffusion [25] and solute diffusion coefficients (Al, Sn, Zn) in Mg [16] calculated in previous works. The vibrational properties are derived from the quasi-harmonic Debye model [26,27]. Therefore, we are able to calculate not only the migration barriers but also the temperature-dependent jump frequencies and the diffusion pre-factors, which are related to vibrational entropic contributions. Finally the dilute solute tracer diffusion coefficients in hcp Mg are calculated. The diffusion pre-factors and the activation energies are obtained by fitting the calculated diffusion coefficients to the Arrhenius-type diffusion equation (see details in Section 2).

The remainder of this paper is organized as follows. In Section 2, a detailed description of diffusion theory in an hcp lattice is provided, including an overview of diffusion equations used in hcp system and the 8-frequency model to calculate the dilute solute tracer diffusion coefficients. The DFT methodology used to calculate the inputs for the diffusion equations and the 8-frequency model is detailed in Section 3. Calculation results are examined in Section 4, followed by a summary in Section 5.

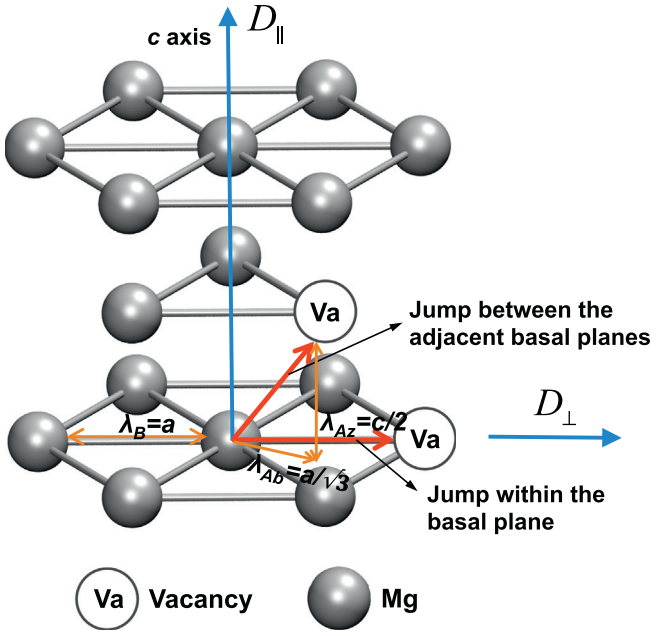

Fig. 2. Illustration of vacancy-mediated diffusion jump components in an hcp lattice showing different jump distances (λ_B, λ_{Ab}, and λ_{Az}). The atom in the middle can exchange position with vacancies (red arrows) either within the same basal plane at a distance of $\lambda_B = a$, or between adjacent basal planes at distances of $\lambda_{Ab} = a/\sqrt{3}$ along the basal plane and $\lambda_{Az} = c/2$ along the c-axis. The jump components along basal plane with jump distances λ_B and λ_{Ab} contribute to the diffusion coefficient $D_{\perp}$ ($\perp$ c-axis), while the jump component along distance λ_{Az} contributes to the diffusion coefficient $D_{\parallel}$ ($\parallel$ c-axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Atomic diffusion theory for hcp lattice

Note that solute diffusion in dilute alloys is also referred to impurity diffusion in the literature [28]. In the remainder of the paper, "solute" is synonymous with "impurity". For the hcp lattice, the crystal anisotropy results in two unique solute jumps, one within the basal plane and the other between adjacent basal planes. These two solute jumps in the hcp structure are illustrated in Fig. 2. This anisotropy leads to two distinctive diffusion tensors. The diffusion coefficient perpendicular to the c-axis, $D_{\perp}$, results from jumps between the adjacent basal planes and jumps within the basal plane; while the diffusion coefficient parallel to the c-axis, $D_{\parallel}$, attributes to jumps between the adjacent basal planes only. Correspondingly, the diffusion coefficients can be calculated using the following equations [29]:

$$D_{\perp} = \frac{1}{2} C_v a^2 \left(3 f_{Bx} \omega_X + f_{Ab} \omega'_X\right) \tag{1}$$

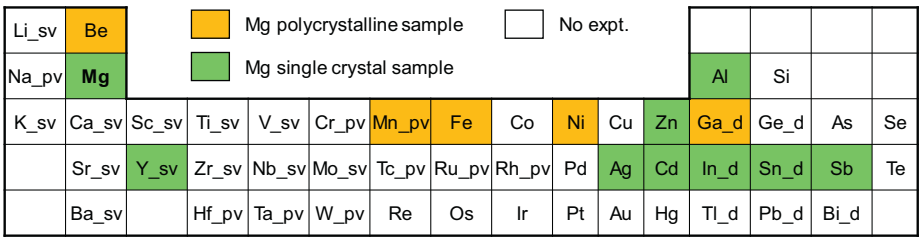

Fig. 1. 49 alloying elements in dilute hcp Mg studied in the present work together with available experiments of diffusion data (see Table 4 for details) denoted in the periodic table. The elemental names indicate the recommended standard potentials supplied by VASP used in the present work for each element. The extensions sv, pv, and d mean the semi-core s, p, and d states are treated as valence states as well, respectively. Note that the diffusion coefficients of Ba and K were not calculated because their direct migration barriers are vanishingly small.