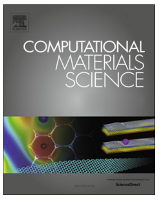
Computational Materials Science 105 (2015) 18–26

Contents lists available at ScienceDirect

Computational Materials Science

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



DFT study on the adsorption and absorption behaviors of liquid nitrogen in the Mg nano alloys synthesized from powder metallurgy

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 10 April 2015
Accepted 15 April 2015
Available online 16 May 2015

Keywords:
Density-functional theory
Cryomilling
Liquid nitrogen
Powder metallurgy
Magnesium nano alloys

ABSTRACT

Mg-based metal-matrix nanocomposites (MMNCs) are lauded as one of the most promising structural materials for vehicle, military, and construction applications. These Mg MMNCs are often synthesized using the powder metallurgy (PM) process under liquid nitrogen cryogenic environments to control the grain sizes. It is believed that proper incorporation of the nitrogen species into the bulk lattice during processing could strongly enhance the mechanical properties of MMNCs by forming N-rich dispersoids. In this work, using the density-functional theory (DFT), we have studied the adsorption and absorption phenomena of liquid nitrogen molecule/atoms that can be applied to the Mg MMNC PM processing. The study includes the impacts of binding sites, alloying elements (Al, Zn, and Y), and surface crystallographic planes on the nitrogen molecule adsorption energies. We also examined the transition state (TS) behaviors for the bond breaking and lattice diffusion of nitrogen. The results show that ~1.13 eV would be required for nitrogen molecule to break the triple bonding and to diffuse into the Mg bulk lattice. Also, it was found that addition of Y can greatly enhance the binding strength of N_2 molecule on the Mg surface.

1. Introduction

Metal-matrix nanocomposites (MMNCs) in which nanosized reinforcements are incorporated in metal-matrix have been investigated in many studies as these materials are thought to potentially possess superior mechanical properties relative to microcomposites because of the nanoparticle (NP)-related contributions to strength, such as (i) the coefficient of thermal expansion (CTE) mismatch strengthening also known as forest strengthening [1], (ii) Orowan strengthening [2], and (iii) grain boundary strengthening as described by the Hall–Petch relation [3]. Reinforcements that consist of ceramic NPs (mostly carbides and oxides), carbon nanotubes, and pure metal NPs may be incorporated in liquid metals by ultrasonic dispersion [4], stir mixing, [5], or stir mixing followed by disintegrated metal deposition (DMD) [6,7]. Various powder metallurgy (PM) techniques have also been broadly used to mix nanosized reinforcements with matrix metal powders [8–11]. Using PM techniques, nanograined metals/alloys can also be used as the matrix, or as a constituent of the matrix. To date, these types of materials including (1) biomodal metallic nanoalloys/MMNCs without reinforcement particles and (2) trimodal MMNCs comprised of coarse grain and nanograined matrix powders with nanosized reinforcements (trimodal MMNCs) have shown the best improvement in yield strength while retaining modest ductility [12–14].

For these bimodal and trimodal MMNCs produced from PM techniques, the nanocrystalline matrix phase is synthesized by a cryomilling process, where the metallic element powders are mechanically milled under a cryogenic environment. Liquid nitrogen is commonly used as a cryogenic media because it can prevent oxidation reactions and grain coarsening during the milling process. In addition, it is believed that the liquid nitrogen can lead to the formation of nitrides or other nitrogen-rich phases (i.e., nitrogen-rich dispersoids), which can act as a source for the Orowan strengthening. It has been observed that concentration of nitrogen in the metal increases with increasing mixing time at cryogenic temperature and also that coarsening of the grains decreases with increasing nitrogen concentration during the higher temperature degassing and consolidation processes [15]. It

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http://dx.doi.org/10.1016/j.commatsci.2015.04.017
0927-0256/

is, therefore, thought that the production of nitrides or other nitrogen-rich phases in the matrix nanograins could be very instrumental in improving the strength of these types of nano alloys/MMNCs as it has been shown that grain size controls the yield stress, ultimate tensile and compressive stress, strain hardening behavior, and strain to failure of bimodal nano alloys [16].

The nitrogen-rich dispersoids that are thought to produce improvements in strength are likely to be the Mg_3N_2 particles, which might be formed on the surface of grains and then could be mechanically introduced to the bulk region of the Mg matrix [17–19]. The free energy of Mg_3N_2 formation is reported as -400.83 kJ/mol at room temperature [20], which presents a suitable thermodynamic stability of nitrogen-rich dispersoids at room temperature after the cryomilling process. Before the formation of these nitrogen-rich dispersoids, it is must be understood that how the nitrogen molecules interact with Mg atoms and other alloying elements in Mg alloys. Despite the vital significance of understanding the interaction between the metal and the liquid nitrogen, the following is not well known: (i) the mechanisms by which the nitrogen atoms/molecules are adsorbed onto the metal surface, (ii) the mechanism by which the nitrogen atoms/molecules are absorbed and diffused into the nanograin matrix, (iii) the nitrogen-rich compounds that are formed, and (iv) the influence of alloying elements on this behavior. In this work, an *in silico* atomistic computational study employing density-functional theory (DFT) has been performed to understand the atomistic interactions between the liquid nitrogen atom/molecule and the nanocrystalline metal matrix. Knowledge of the interaction of the liquid nitrogen with the surface is essential to understand the nitrogen incorporation process of nanocrystalline Mg alloys synthesized using PM. In particular, Mg-based nanocrystalline materials were selected in this work, as nanograined Mg alloys/MMNCs are considered as one of the most promising candidates to replace the traditional heavy structural materials/composites and they are widely fabricated using PM techniques [21]. The objectives of the present study are to (i) understand the atomistic mechanism of nitrogen adsorption onto the Mg surface, (ii) understand the impacts of alloying and impurity elements in Mg alloys on nitrogen adsorption, and (iii) understand the absorption behavior and bulk interaction of N and N_2 with Mg materials. The impacts of impurity elements such Al, Zn, and Y were examined because these elements are incorporated in the nominal compositions of AZ31 (Mg-3%Al-1%Zn) and WE43 (Mg-4%Y-3.5RE) alloys, which are commonly used as the nano crystalline metal-matrix for Mg-based nanograined alloys/MMNCs synthesized from PM.

2. Computational methods

DFT calculations were performed to estimate the energy of the system in the most stable electronic state using the DMol3 module in Materials Studio package (version 7.0, Accelrys Inc.) [22,23]. Adsorption behavior of molecular nitrogen (N_2) and bulk interaction (structural stability) of both atomic and molecular nitrogen (N and N_2) on a Mg $4 \times 4 \times 2$ supercell with 30 Å vacuum space and coverage of 0.0625 monolayer (ML) were studied by treating exchange–correlation energy with PW91 functional in the GGA scheme. Impacts of different crystallographic surface structure were compared using the Mg systems with basal (0001), prism $(10\bar{1}0)$, and pyramidal $(\bar{1}01\bar{1})$ surface planes. Fig. 1 presents the DFT slab models with periodic boundary conditions containing (a) basal, (b) prism, and (c) pyramidal surfaces, and (d) the schematic illustration for the positions of these planes in a hcp crystal structure. The double-numeric quality basis set plus polarization with all electron core treatment was utilized in our model. In all of the computations, the Fermi smearing value of 0.007 Ha (1 Ha = 27.2114 eV) and a real-space cutoff of 4.9 Å were used to improve the computational performance, and the self-consistent iteration tolerance of 10^{-6} was applied. The charge and spin was chosen to be 0.05 for density of mixing and the dipole slab correction was applied to accelerate the convergence. To represent the surface and bulk components of crystals, one bottom layer was fixed and the rest of the layers were free to relax in all the geometry optimization computations. For the convergence condition in geometry optimizations, the tolerances were considered to be 10^{-5} Ha for energy, 2×10^{-3} Ha/Å for force gradient, and 5×10^{-3} Å for displacement. A $(2 \times 2 \times 1)$ *k*-point set was used and the adsorption energy (E_{ad}) was calculated from the difference between the energies of the combined structure of Mg/N_2 molecule and the separated structures of isolated adsorbent and adsorbate. In studying the adsorption behavior of N_2 on different sites over the Mg surface, the vibrational frequencies for the surface-N_2 (ν_{N-S}) and the intermolecular N–N stretching modes (ν_{N-N}) were computed using a finite-difference method. During the vibrational computations, the Mg substrate was frozen while the N_2 molecule was free to vibrate in any direction. In addition to the adsorption behavior of liquid nitrogen onto the Mg alloy surfaces, the structural stability of the Mg was evaluated by calculating the energy of the system with N_2 molecule or N element absorbed in the bulk material. The structural stability was studied by comparing the energies of the system for separate parts and the final combined configuration.

3. Results and discussion

3.1. Surface energies

The surface energies of Mg/Mg alloys were first calculated to examine the impacts of surface crystal orientation and the impurity elements. The surface energy, γ, for pure Mg materials can be typically calculated by the following equation,

$$\gamma_{\text{pure}} = \frac{E_{\text{Mg}}^{\text{slab,relaxed}} - 0.5 n_{\text{Mg}} E_{\text{Mg}}^{\text{bulk}} - 0.5 E_{\text{Mg}}^{\text{slab,unrelaxed}}}{A} \tag{1}$$

where $E_{\text{Mg}}^{\text{slab,relaxed}}$ is the total energy of the vacuum slab after the geometry optimization, $E_{\text{Mg}}^{\text{bulk}}$ is the total energy of bulk Mg unit cell, n_{Mg} is the ratio of the number of atoms in the slab to the Mg unit cell, $E_{\text{Mg}}^{\text{slab,unrelaxed}}$ is the total energy of the vacuum slab without geometry optimization (i.e., all atomistic positions are fixed), and A is the surface area in the slab, respectively. Note that Eq. (1) is used to calculate γ of relaxed surface only, while $\gamma_{\text{pure}} = \frac{E_{\text{Mg}}^{\text{slab,relaxed}} - n_{\text{Mg}} E_{\text{Mg}}^{\text{bulk}}}{2A}$ is typically used to calculate the average γ of unrelaxed and relaxed surfaces. For the surface energy computations including an impurity element (e.g., Al, Zn, or Y) on the surface, one middle Mg atom on the (0001) surface was replaced by one of the three alloying elements. When an alloying element is incorporated onto the Mg surface, the expression for the surface energy, γ, of the alloyed surface must be modified and is expressed in Eq. (2),

$$\gamma_{\text{alloy}} = \frac{E_{\text{Mg-alloy}}^{\text{slab,relaxed}} - 0.5 n_{\text{Mg}} E_{\text{Mg}}^{\text{bulk}} - 0.5 n_{\text{alloy}} E_{\text{alloy}}^{\text{bulk}} - 0.5 E_{\text{Mg -alloy}}^{\text{slab,unrelaxed}}}{A} \tag{2}$$

where $E_{\text{Mg -alloy}}^{\text{slab,relaxed}}$ is the total energy of the vacuum slab including an alloying element after the geometry optimization, $E_{\text{Mg}}^{\text{bulk}}$ is the total energy of bulk Mg unit cell, n_{Mg} is the ratio of the number of atoms in the slab to the unit cell, $E_{\text{alloy}}^{\text{bulk}}$ is the total energy of bulk unit cell of alloying element, n_{alloy} is the ratio of the number of atoms in the