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Nanostructured BN – Mg Composite: Features of Interface Bonding and Mechanical Properties

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Magnesium (Mg) is one of the lightest industrially used metals. However, wide applications of Mg-based components require substantial enhancement of their mechanical characteristics. This can be achieved by introducing small particles or fibers into the metal matrix. Using first-principles calculations, we investigate the stability and mechanical properties of a nanocomposite made of magnesium reinforced with boron nitride (BN) nanostructures (BN nanotubes and BN monolayers). We show that boron vacancies at the BN/Mg interface lead to a substantial increase in BN/Mg bonding establishing an efficient route towards the development of BN/Mg composite materials with enhanced mechanical properties.

Introduction

Together with Lithium, Magnesium is the lightest material among the metals used in industry having a density of only 1.7 g/cm^3. Due to its low weight and good casting properties, Mg and its alloys are used in many technologies. For example, the use of Mg alloys in the automotive, aviation and aerospace industries leads to significant savings in fuel and, consequently, to a decrease in emissions.[1] However, as compared with other structural materials, magnesium displays low strength and poor workability related to its notable brittleness, which significantly limits the application fields. It is known that an increase in mechanical strength of a material may be achieved through introducing small particles or fibers into the metal matrix. It is also worth noting that composite materials based on magnesium are 30% lighter than similar materials based on aluminum.[2] Such materials are thought to also display good specific properties and stable linear thermal expansion coefficient in a wide temperature range, which can be adjusted while choosing a particular combination of the matrix and filler characteristics.

A number of papers has been devoted to the synthesis of composites based on Mg with BN nanoparticles aimed at the improving mechanical and structural characteristics of the metal matrix. Using a powder metallurgy route the composites with improved mechanical properties were obtained, as revealed by micro-indentation, tension and compression tests.[3,4] It was found that increasing the BN nanoparticle contents had led to decreasing a compression fracture strain and increasing a tensile fracture force.

Using hexagonal boron nitride (*h*-BN) nanofilms or nanotubes as the regarded fillers has a number of advantages. BN nanotubes (BNNTs) and two-dimensional (2D) BN sheets have extremely high Young's modulus (~1 TPa)[5] comparable to their carbon-based counterparts, i.e. carbon nanotubes and graphene, which are known to be the stiffest materials on Earth. Moreover, the surface of *h*-BN is chemically inert, this, on one hand, prevents the reinforcement agents from sticking together, and provides their spatially uniform distribution in a composite, but, on the other hand, does not allow BN nanostructures to effectively bind to the metal matrix. Thus, the investigation of binding features of *h*-BN/Mg interfaces is highly important and timely-warrant for the further development of new generation of lightweight and strong composites.

Herein, using *ab initio* calculations we studied in details the interfacial properties of *h*-BN based nanostructures (BNNTs and single-layered *h*-BN) embedded into a Mg matrix. We modeled a composite materials based on BNNT fixed into such matrix and *h*-BN sandwiched between atomically-thin Mg slabs with different surfaces and stackings. We found that BN surface interacts with low-energy and low-index Mg surfaces in substantially different ways. We showed that introduction of boron vacancies leads to a substantial increase in the interfacial strength. It was found that the presence of Mg surfaces from both sides of a *h*-BN sheet results in significant

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enhancement of composite shear stress dependent on the type of Mg surface. The results of our study devoted to the bonding details at the *h*-BN/Mg interfaces, as well as the estimation of critical shear stress, indicate that mechanical characteristics of *h*-BN/Mg composites can be substantially improved in the following-up experiments.

Computational details

All calculations of the atomic structure, binding at the Mg/BN interfaces and mechanical properties of the whole *h*-BN/Mg composite were performed using a density functional theory (DFT) within the PBE-PAW [6] approximation including non local van der Waals component [7,8] with the periodic boundary conditions, as implemented in the Vienna *ab-initio* Simulation Package.[9,10] The plane-wave energy cutoff was equal to 450 eV. To calculate the equilibrium atomic structures, the Brillouin zone was sampled according to the Monkhorst–Pack scheme [11] with a grid 2×2×1 k-point. To avoid the interaction between the neighboring layers, the vacuum space between them was set larger than 20 Å. A similar simulation setup has been used before to model the graphene/Ir interface. [12-14] The structural relaxation was performed until the forces acting on each atom were less than 0.001 eV/Å. Before starting calculations of graphene on Mg surface, we tested the selected approach and found that the DFT-PBE approximation including non local van der Waals component well described the system of interest. We found that the lattice constants of Mg and *h*-BN, predicted as 3.19 Å and 2.51 Å, respectively, well match the experimental data of 3.22 Å [15], 3.20 Å [16] and 2.50 Å. [17] The model of pristine surfaces of *h*-BN/$(10\bar{1}0)$Mg composite considered in our work consisted of 160 Mg atoms (5 layers in the slab) and 80 atoms in *h*-BN forming a rectangle supercell. In case of (0001)Mg surface the supercell consisted of 48 Mg atoms (3 layers in the slab) and 50 atoms in *h*-BN. Test calculations showed that increasing the number of layers in the Mg slab beyond 3 had given rise to only negligible changes in the binding energy (less than 0.5 meV/Å^2). In order to avoid artificial strain in the system originating from the lattice mismatches between *h*-BN and Mg substrates, the specific supercells were constructed and analyzed (namely, 4×4 *h*-BN unit cells with 3×3 Mg(0001) unit cell, and 3×5 h-BN unit cells with 2×4 Mg$(10\bar{1}0)$ unit cells,) under the conditions that the difference between the Mg and *h*-BN lattices was less that 2% in each direction. Increasing the supercell size led to minor changes in the binding energies, i.e. less than 0.8 meV/Å^2.

In this work we focus on the estimation of the critical shear stress as one of the most important parameters in macroscopic models of composite materials, such as nanotube-metal composites [18] or nanotube networks. [19] The shear stress was calculated by moving the *h*-BN sheet stepwise along the armchair direction. For each step the geometry optimization and total energy calculations were performed. Then the critical shear stress, τ_c, was defined as the maximum force along the moving direction divided by the surface area. We assumed that during Mg/BNNT or Mg/*h*-BN preparation the nanostructures had been distributed uniformly and isotropically in the metal matrix, which would lead to the isotropic improvement of the composite mechanical characteristics.

Results and discussion

We considered the two general cases represented by two nanostructure ensembles: *h*-BN/Mg - as the interface between Mg and the outer BNNT surface, and Mg/*h*-BN/Mg - as the interfaces between *h*-BN monolayer embedded into the metal matrix. The total binding energy at the interface was defined as: $E_b^{tot} = E[\mathrm{A+B}] - E[\mathrm{A}] - E[\mathrm{B}]$, where $E[\mathrm{A+B}]$ is the energy of whole structure, and $E[\mathrm{A}]$ and $E[\mathrm{B}]$ are the energies of constituent parts A (metal slab) and B (*h*-BN).

Composite materials based on Mg were formed by mixing of filler nanoparticles in liquid Mg, which can lead to the interface formation with different Mg surfaces. Here we considered two low-energy and low-index surfaces, namely (0001) and $(10\bar{1}0)$, as presented in Figure 1 a and Figure 1 b, respectively.

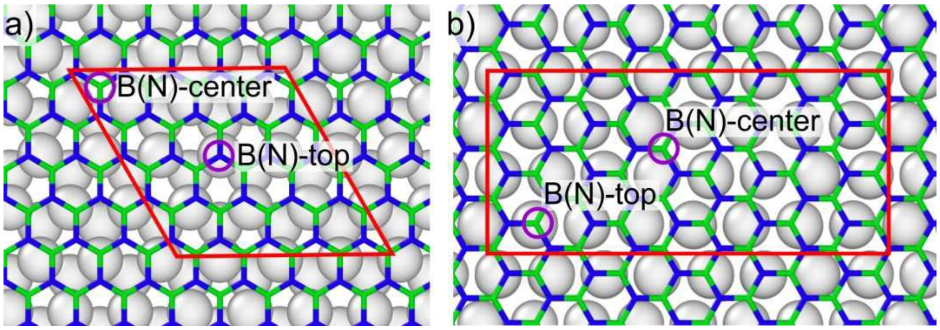

Figure 1 Atomic structure of BNNT surface located on (0001) (a) and $(10\bar{1}0)$ (b) Mg surfaces; Simulated supercell is depicted by red frames; positions of vacancy defects created by removing B and N atoms at top and center positions are denoted by purple circles. Nitrogen, boron and magnesium atoms are depicted in blue, green and grey colors, respectively.

In the experiments, BN nanostructures used for filling the metals have a mean size of more than 50 nm. As for BNNTs, their small curvature and natural polygonal [20] cross-sectional morphology imply that BNNTs at the interface with Mg can be modelled as a flat *h*-BN layer representing the outer BN surface.

We found that the binding energy between BN and (0001)Mg surfaces is -9.31 meV/Å^2. Such binding is of the order of the electrostatic interaction of BN with Al (-14 meV/Å^2 [21]) and much smaller than the interaction of BN with Ru (-55 meV/Å^2, [22] -66 meV/Å^2 [21]). This result is in line with the experimental observation that (0001)Mg is less reactive among other Mg surfaces. [23] One can expect that other surface orientations can be more favorable for the formation of the strong interface with BNNT. We estimated the most important mechanical characteristic of the composite, i.e. critical shear stress, τ_c, from the energy-BN displacement dependence. Our calculations gave a value of ~28 MPa, which is insufficiently low for making a strong composite. This result allows us to conclude that BN displays low wettability on the (0001)Mg surfaces.

The interaction of BN with $(10\bar{1}0)$Mg surface is stronger. E_b^{tot} in this case equals to -16.17 meV/Å^2. The critical shear stress, τ_c, is also higher (~47 MPa), therefore, a BN/Mg composite, in which interfaces with both surfaces can be created, would display enhanced but still insufficient mechanical characteristics.

The usual way of increasing nanostructures' wettability is the creation of defects in them. [24-28] We investigated this effect in the context of BN surface with vacancies. Such defects can eventually appear during the preparation of the composites. The Moiré structure of the interface assumes a number of nonequivalent positions of defects in the supercell. We focused our analysis on the limiting cases, i.e., vacancies created in high-symmetry areas at the interface: directly on top of Mg atom in the first layer of the slab titled, B(N)-top, and directly between Mg atoms in the slab tilted, B(N)-center (Figure 2). Energies of defects in the intermediate positions are expected to be within the energy range defined by the limiting cases. The defects can also be distinguished by their location in the BN lattice (B or N).

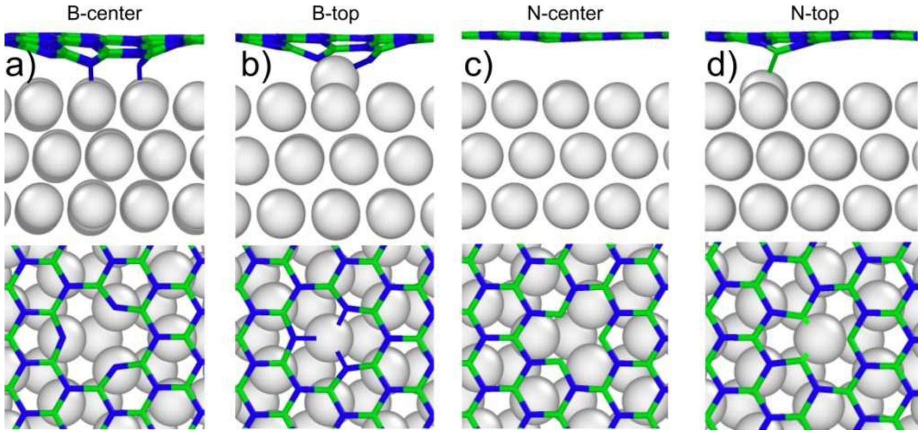

Figure 2 Atomic configurations of (0001) Mg/BNNT interface with boron (a, b) and nitrogen (c, d) vacancies at the center (a, c) and top (b, d) positions. Nitrogen, boron and magnesium atoms are depicted in blue, green and grey colors, respectively.

It was found that B-vacancies result in a sufficient increase in the interaction between the BNNT and Mg surfaces. The presence of lone-electron pairs in the neighboring nitrogen atoms leads to the attraction of the underlying Mg atom, which, however, embeds in BN surface only partly due to a larger atomic size of Mg than that of missing B atom in all cases, except for B-center positions for the (0001)Mg surface. This indicates that formation energy of surface vacancy in Mg is very small. The presence of boron vacancy in both B-center and B-top positions gives rise to a sufficient increase in critical shear stress, τ_c (~1 GPa and ~500 MPa for (0001) and $(10\bar{1}0)$ Mg surface, respectively, for the given defect concentration), which clearly points to the formation of rigid BNNT/Mg interface. The presence of N vacancies practically does not influence the surface structure due to electron deficit in the neighboring B atoms, and does not form the bond at the interface. Therefore, this only slightly improves the mechanical properties of the interface with respect to the pristine system: τ_c becomes about ~100 MPa and more than 110 MPa for (0001)Mg and $(10\bar{1}0)$Mg surfaces, respectively, at both N-center and N-top positions. This data are summarized in Table 1.

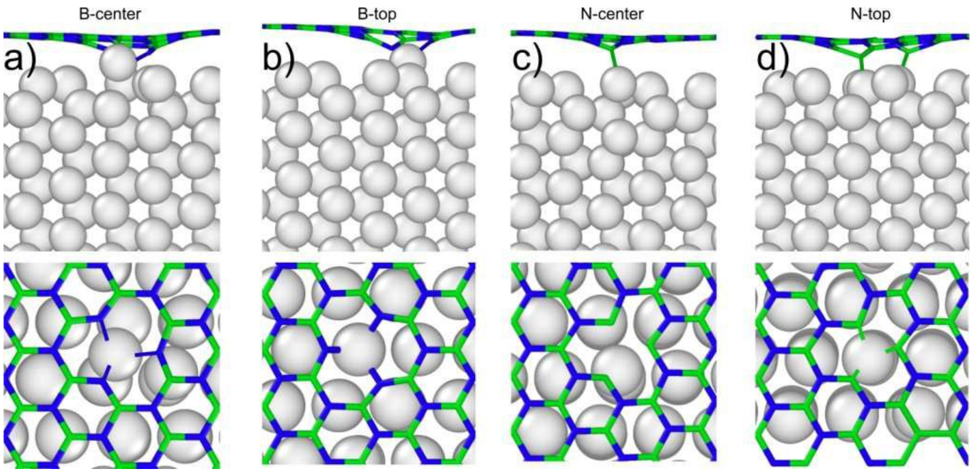

Figure 3 Atomic configurations of $(10\bar{1}0)$Mg/BNNT with boron (a, b) and nitrogen (c, d) vacancies at center (a, c) and top (b, d) positions. Nitrogen, boron and magnesium atoms are depicted in blue, green and grey colors, respectively.

Table 1 Binding energies between Mg surfaces of different orientations and pristine BNNT surfaces and with those having vacancy defects, and the corresponding critical shear stresses.

Defect type	Binding energy, meV/Å^2		τ_c, MPa	
	(0001)	$(10\bar{1}0)$	(0001)	$(10\bar{1}0)$
B-center	-53.01	-44.52	925.09	583.56
B-top	-57.24	-47.63	$1.15\cdot10^3$	502.31
N-center	-13.02	-16.31	77.19	119.84
N-top	-15.2	-17.18	110.56	155.56
Pristine interface	-9.31	-16.17	27.93	47.29

If we take into account a relatively weak decrease in *h*-BN stiffness with increasing vacancy defects concentration, [21] the composite should display enhanced mechanical characteristics. Further, we focused on the properties of a single *h*-BN sheet embedded into the metal matrix. Surrounding of BN monolayer by metal from both sides allows us to expect two times stronger binding due to the doubled area of the accessible surface. As in the previous case, we considered two different Mg surface orientations: $(10\bar{1}0)$Mg (Figure 4a) and (0001)Mg (Figure 4 b). Interactions of *h*-BN with two possible stacked surface layers were studied.

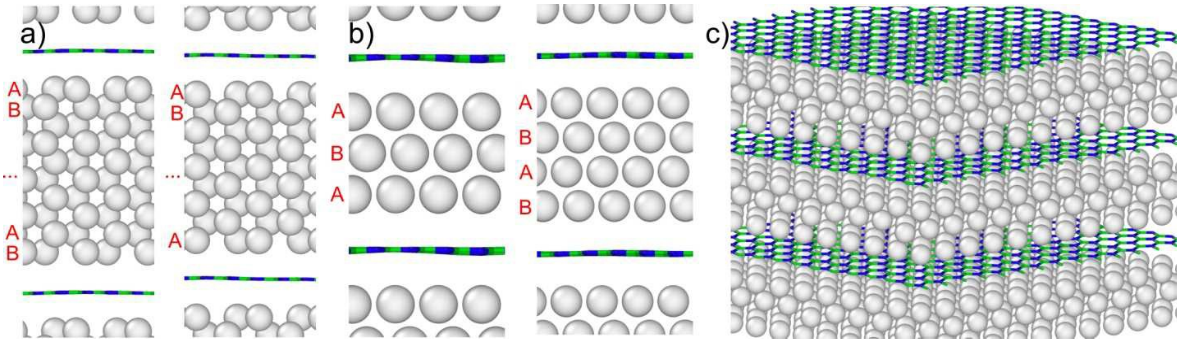

Figure 4 Atomic geometry of a composite based on individual *h*-BN sheets embedded between Mg matrix slabs with (a) $(10\bar{1}0)$ and (b) (0001) Mg surfaces. (c) Schematic 3D view of the composite. Nitrogen, boron and magnesium atoms are depicted in blue, green and grey colors, respectively. Red letters define layer stacking.

We obtained a similar dependence on the Mg surface orientation. In the case of $(10\bar{1}0)$Mg and (0001)Mg orientations the binding energies of ~-40 meV/Å^2 and ~-20 meV/Å^2 were computed. The presence of Mg surfaces on both sides of *h*-BN sheet also improves the interface mechanical properties to ~100 MPa (~130 MPa) for Mg$(10\bar{1}0)_A$/*h*-BN/Mg$(10\bar{1}0)_A$ (Mg$(10\bar{1}0)_A$/*h*-BN/Mg$(10\bar{1}0)_B$) and to ~100 MPa (~200 MPa) for Mg(0001)$_A$/*h*-BN/Mg(0001)$_A$ (Mg(0001)$_A$/*h*-BN/Mg(0001)$_B$) interfaces, respectively. The calculated binding energies are summarized in Table 2. It should be noted that even though we observed correlations between binding energy and critical shear stress (τ_c), the relationship between these two quantities is not trivial and depends on the type of the surface.

Table 2 Binding energies between Mg/*h*-BN/Mg slabs with A and B stackings and their relative critical shear stresses

Interface type	Binding energy, meV/Å^2	τ_c, MPa
Mg$(10\bar{1}0)_A$/*h*-BN/Mg$(10\bar{1}0)_A$	-43.05	98.29
Mg$(10\bar{1}0)_A$/*h*-BN/Mg$(10\bar{1}0)_B$	-43.75	126.13
Mg(0001)$_A$/*h*-BN/Mg(0001)$_A$	-16.38	104.39
Mg(0001)$_A$/*h*-BN/Mg(0001)$_B$	-20.31	206.02

Conclusions

To sum up, the investigations of interface stability and mechanical properties of a nanocomposite material consisting of *h*-BN nanostructures embedded into magnesium matrix were carried out within the framework of DFT calculations. It was found that nanostructured BN with pristine surface cannot be used as a filler for reinforcing magnesium due to its low wettability on low energy (0001) and $(10\bar{1}0)$ Mg surfaces. The presence of B-vacancy defect improves mechanical properties (critical shear stress) of the composite and leads to the formation of strong interface between BN and Mg surfaces, whereas N-vacancy defects do not lead to mechanical characteristics improvement. Additional investigations of a composite material based on individual *h*-BN sheet sandwiched between Mg surfaces show that surrounding of BN monolayer by metal from the both sides leads to two-times increase in the interface binding energy due to doubling of the area of the accessible surface, as well as to improving the mechanical properties of the composite. Our preliminary studies also indicate that oxygen atoms present at the interface may also affect the adhesion and critical shear stress, but the quantitative assessment of the effects of oxygen is beyond the scope of this work.

As intensive industrial developments require the fabrication of novel materials with improved mechanical characteristics, and because nanocomposites based on Mg matrices reinforced with nano-BNs should combine the light weight of Mg and superb mechanical properties of BN nanostructures, we believe that the development of such materials with a combination of unique characteristics is important for future progress in diverse industrial fields, such as aerospace and automobile industries.

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