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Interface relationship between TiN and Ti substrate by first-principles calculation

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ABSTRACT

In this paper, the lattice misfits between Ti and TiN interfaces were calculated by the Bramfitt two-dimensional lattice misfit theory. The adhesive work (W_{ad}), interfacial energy (γ), electronic property and bonding characteristic of Ti(0 0 0 1)/TiN(1 1 1) interface were also investigated by first-principles calculation. The results show that, the lattice misfit of Ti(0 0 0 1)/TiN(1 1 1) interface is only 2.46%, which indicates that Ti(0 0 0 1) and TiN(1 1 1) faces can make good lattice matching. Based on three atomic stacking modes (OT-, SL- and TL-sites) and two terminations of TiN(1 1 1) face, six kinds of Ti(0 0 0 1)/TiN(1 1 1) interface models were established. The interfacial bonding strength and stability of the Ti(0 0 0 1)/TiN(1 1 1) N-terminated (Ti/N) interface models are all larger than those of Ti(0 0 0 1)/TiN(1 1 1) Ti-terminated (Ti/Ti) ones. W_{ad} of the N-TL interface (Ti structure contacting with N-terminated structure of TiN with TL site) is the largest (7.97 J/m^2), while the relaxed interfacial separation (d_0) is the smallest (1.181 Å) and the γ is the smallest (−3.86 J/m^2), which indicates that the bonding strength and stability of the N-TL interface are the largest in all interface models. Additionally, the interface bonds of Ti/Ti interface models are weak, and their interfacial strength and stability are relatively weak. The bonding strengths of the three interface models of Ti/N interfaces are larger than that of the Ti/Ti interfaces, which forms a strong polar covalent bond and a metallic one.

1. Introduction

Because of high specific strength, fracture toughness, corrosion resistance and thermal stability, titanium alloys have been applied for biomedical, aerospace and extreme mechanical applications and other fields [1–3]. However, because of their low hardness and wear-resistance, their application on the wear-resistance field has been restricted. Therefore, it is significant to prepare a wear resistance coating on the surface of titanium alloys.

At present, surface hardening of titanium alloys includes spraying, laser and physical vapor deposition. Koshuro et al. [4] prepared the metal oxide coating on the VT6 titanium alloy by plasma spraying and micro-arc discharges, and the changes in the composition, structure and mechanical properties of the metal oxide coating were studied, which found that the microhardness of the coating is increased from 1013 ± 150 HV to 1639 ± 31 HV. Diao et al. [5] prepared TiC/TiB_2 composite coating on TC2 titanium alloy by laser cladding method, and studied its microhardness and corrosion resistance of TC2 titanium alloy, which indicated that the hardness of the coating is three times higher than that of the TC2 alloy matrix, and the corrosion resistance of the coating is obviously higher than that of the TC2 titanium alloy matrix. Marin et al. [6] deposited CrN and TiCN coating on the surface of TC4 titanium alloy by magnetron sputtering, and took carburizing and nitriding treatment to the coating, which found that the coating after carburizing and nitriding treatment can significantly improve the tribological properties of the titanium alloy coating.

In recent years, because of its high melting point, high hardness, low friction coefficient and strong corrosion resistance, TiN has been used as a surface coating for titanium alloy workpieces widely. Kim et al. [7] investigated the effect of TiN coating on the corrosion of nano-structure Ti-30Ta-xZr alloy, which showed that the corrosion resistance of the TiN coating is higher than that of the untreated titanium alloy. Lin et al. [8] prepared TiN coating on Ti6Al4V titanium alloy and researched the effect of TiN coating on the adhesion and corrosion resistance of bacteria, which indicated that the continuous compact coating could significantly reduce the bacterial adhesion and corrosion resistance of the

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Ti6Al4V substrate. Feng et al. [9] prepared the reactive plasma sprayed TiN coating and studied the friction properties of the TiN coating, which showed that the RPS-TiN coating is better than the high speed steel in the non-lubrication condition and the volume wear of the TiN coating is 2/5 of the M2 steel. However, because the TiN coating on the surface of titanium alloy workpieces is too thin, it is difficult to evaluate the binding properties by experimental method.

First-principles calculation can be used to reveal the atomic and electronic structures of interfaces, as well as the stability and cohesion of interfaces, which is widely used in material calculation [10,11]. Xiong et al. [12] calculated the interface bonding work, interfacial energy, the interface electronic structure and bonding properties of the composite coating TiB_2/TiC interface by first-principles, which showed that C/Ti-terminated hollow stack (C-HS-T) exhibits the largest W_{ad} (11.43 J/m^2), the smallest interfacial separation d_0 (1.208 Å), which indicated that C/Ti-terminated hollow stack (C-HS-T) is the most stable. Fan et al. [13] studied the bonding and electronic properties of TiC(1 1 1)/TiN(1 1 1) interface, which indicated that the bonding properties at the interface are very similar to those of the bulk material, and the electronic transition at the interface is smooth. Liu et al. [14] calculated the electronic structure and bonding characteristic of TaN (1 1 1)/TiN(1 1 1) interface, and studied the bonding and stability of TaN(1 1 1)/TiN(1 1 1) interface as well as the bonding of atoms at the interface. However, the bonding properties between TiN coating and titanium alloy substrate by first principles calculation has not been reported before.

On the basis of the Bramfitt two-dimensional lattice misfit theory, the best interface between the TiN coating and the Ti substrate for lattice matching was selected, the first principles method based on the density functional theory (DFT) was used to calculate the adhesive work, interfacial energy, electronic property and bonding characteristic of Ti(0 0 0 1)/TiN(1 1 1) interface in order to study the bonding of Ti/TiN interface theoretically.

2. Calculation method

First-principles calculation based on DFT was carried out by the Vienna ab initio simulation package (VASP) [15] with the projector augmented wave (PAW) [16] method. The generalized gradient approximations (GGA) functional of Perdew-Burke-Ernzerhof (PBE) [17] were used to describe the exchange-correlation energy. For the pseudopotential, the electronic configurations are [He]$2s^2 2p^3$ and [Ar] $3d^2 4s^2$ for nitrogen and titanium, respectively. The models used in the calculations are single unit cells of Ti bulk (1 × 1) and TiN bulk (1 × 1). In order to ensure the accuracy of the calculation, the convergence test for Kpoints and atomic wave function energy cutoff (Encut) are carried out. The Kpoints was acquired by Monkhorst-Pack method [18]. The convergence standard is that the change of the energy is less than 0.001 eV/atom between former and later energies.

After a series of convergence tests (see Supplementary Figs. 1 and 2), Encut for bulk and surface calculations are set as 450 eV for Ti and 400 eV for TiN, while those for interface calculations are set as 450 eV. K points of 10 × 10 × 7, 12 × 12 × 12, 10 × 10 × 1, 12 × 12 × 1 and 12 × 12 × 1, are used for calculations for bulk Ti, bulk TiN, Ti surface, TiN surface and Ti/TiN interface, respectively. Energy change convergence value is less than 1.0×10^{-5} eV/atom.

3. Results and discussion

3.1. Bulk property

In order to verify the reliability of the calculation method, the GGA-PBE algorithm was used to calculate the bulk properties of TiN, including lattice constants, bulk modulus (K) and formation energy (E_{for}), The lattice constants and bulk modulus of TiN can be obtained directly from the calculated results. The E_{for} can be obtained from the following formula Eq. (1) [19]:

$$E_{for}^{TiN} = \frac{1}{N_{TiN}}(E_{TiN}^{bulk} - E_{Ti}^{bulk} - E_{N}^{bulk}) \quad (1)$$

where E_{for}^{TiN} is the formation energy of the bulk TiN; E_{TiN}^{bulk} is the total energy of the bulk TiN; E_{Ti}^{bulk} and E_{N}^{bulk} are the energy of a Ti atom and a N atom in a single Ti, N system, respectively. Here the energy of the Ti atom in the α-Ti and the N atom in the nitrogen molecule were employed to take the place of E_{Ti}^{bulk} and E_{N}^{bulk}, respectively. N_{TiN} is the numbers of atoms in one TiN unit cell.

Table 1
Calculated results of relaxed TiN bulk compared with other published papers.

System	Method	Lattice constants a (Å)	Bulk modulus K (GPa)	Formation energy E_{for} (GPa)
TiN		4.24	308.39	−3.50
	GGA-PBE[a]	4.25	266	−3.94
	GGA-PW91[b]	4.245	279.15	–
	LDA-FLAPW[c]	4.18	329	−4.36
	Expt	4.24[d]	320[c]	−3.50[e]

[a] Ref. [13].
[b] Ref. [14].
[c] Ref. [20].
[d] Ref. [21].
[e] Ref. [22].

The calculation results of lattice constants, K and E_{for} of bulk TiN as well as the results of other literature [13,20–23], are listed in Table 1. From Table 1, the calculated results of TiN are in agreement with the calculated ones in other literature, and with the experimental ones, which indicates that the GGA-PBE algorithm can fully guarantee the accuracy of the calculation results.

In order to ensure the stability of the structure used in the calculation, the crystal structures of Ti and TiN are fully relaxed. The crystal structures of Ti and TiN are shown in Fig. 1. Ti structure is close-packed hexagonal one with the space group of P63/mmc (1 9 4), as shown in Fig. 1(a). The optimized primitive lattice parameters (a = 2.923 Å and c = 4.631 Å) are in good agreement with other experimental values (a = 2.951 Å, c = 4.686 Å [23]), which proves a good accuracy of the calculation with an error limit of 10^{-2} Å. From Fig. 1(b), TiN lattice structure is NaCl-type one with the space group Fm−3m (2 2 5). The lattice constant of TiN after optimization is 4.238 Å, which is basically the same as the measurement result (a = 4.24 Å) in Ref. [21] and the calculation result (a = 4.33 Å) in Ref. [13].

3.1.1. Bulk property of TiN

The band structure and density of states (DOS) of bulk TiN are shown in Fig. 2. Fig. 2(a) is the band structure of TiN, in which some bands passes through the Fermi level. It indicates that TiN is of metallic character. Fig. 2(b) is the DOS of TiN. From the total DOS of TiN, two peaks at the two sides of Fermi level are located near −5.45 eV and 2.15 eV, respectively, and the DOS between two peaks is not zero, which indicates the formation of covalent bonds. In addition, there is electron states around Fermi level, which indicates that TiN has a certain metallic character. By analysis of partial density of states (PDOS) in Fig. 2(b), it is seen that from −8 eV to Fermi level, the peak patterns of Ti-3d electron orbital are basically the same as N-2p electron orbital, which indicates that the two orbitals overlap and form a strong covalent bond. From −16.7 eV to −14.9 eV, Ti-3d orbital interacts with N-2s orbital weakly, which also has a certain contribution to the covalent bonds. From the above analysis, the bonding of TiN is a mixture of metallic bond and polar covalent one.

The calculation of the elastic constants for bulk TiN is helpful to study the mechanical properties of TiN. The calculated results of elastic stiffness constant (C_{ij}) for TiN crystal structure are as follows: