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First-principles calculations on the electronic structure and cohesive properties of titanium stannides

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ABSTRACT

First-principles calculations based on the density-functional theory were employed to investigate the electronic structure and cohesive properties of Ti–Sn alloys. Based on the calculated results, the lattice constants, bulk modulus and formation energies for the Ti–Sn intermetallics were compared with previous experimental and theoretical investigations. It was demonstrated that in term of the means volume and cohesive properties, the structure stability of Ti–Sn intermetallics increased with decreasing Ti composition, which was also supported by the analysis of densities of states. Furthermore, it was found that the difference in stability between the Ti–Sn intermetallics could be attributed to the bonding electron numbers at the upper region of the valence-band complex, which was cut by Fermi level. In addition, the electronic structure of the Ti–Sn intermetallics also showed a strong hybridization between Ti 3d and Sn 5p states, which played a dominant role in the bonding mechanism of Ti_3Sn and Ti_2Sn.

1. Introduction

Titanium alloys are becoming more and more important in various industrial applications as lightweight structural materials—from medical instruments to aerospace industry because of their low density, outstanding mechanical properties, excellent corrosion and oxidation resistances, etc. [1,2]. Over the past decades, the main research on such alloys has focused on the improvement of their comprehensive properties and the extension of their practical applications. To this end, alloying has been considered as one of the most effective ways. Tin is a common and important alloying element and can significantly increase the strength and corrosion resistance of Ti alloys, and particularly, produce additional properties such as superconductivity and magnetism. Suiter [3] and Kornilov and Nartova [4] investigated the effect of Sn additives on the mechanical properties of pure titanium, and found a remarkable increase in strength by alloying of 3–6 at.% Sn at room temperatures. Drymiotis et al. [5] showed that β-Ti_6Sn_5 compound had an unusual magnetic characteristics.

Experimental investigations indicated that in the Ti–Sn binary system, there were five intermetallic compounds, i.e., Ti_3Sn, Ti_2Sn, Ti_5Sn_3, α-Ti_6Sn_5, β-Ti_6Sn_5 [6], and the stable phases are α-Ti_6Sn_5 and β-Ti_6Sn_5 for low and high temperatures, respectively. It is interesting to note that recently Kuper et al. [7] found a formerly unknown stable phase for Ti_2Sn_3 and subsequently Künnen et al. [8] and Kleinke et al. [9] revealed that its crystal structure was hexagonal. However, compared to the above experimental investigations and measurements, theoretical studies on this aspect were very few. Especially, to date first-principles calculation on the electronic structure of Ti–Sn compounds has never been conducted. This makes it difficult to investigate thoroughly their microstructural evolution and to understand comprehensively their macroscopic behavior, e.g., mechanical properties.

In the present study, a first-principles calculation based on the density-functional theory was conducted to investigate the electronic structure and cohesive properties of Ti_3Sn, Ti_2Sn, Ti_5Sn_3, Ti_6Sn_5 and Ti_2Sn_3 in this alloy system. The stability of these compounds was analyzed, and the bonding mechanism in Ti_3Sn and Ti_2Sn alloys was further discussed as a typical example.

2. Models and computational method

The lattice structures for the 6 intermetallics, i.e., Ti_3Sn, Ti_2Sn, α-Ti_6Sn_5, α-Ti_6Sn_5, Ti_5Sn_3 and Ti_2Sn_3 in the binary Ti–Sn system are *hP*2, *cF*8, *hP*8, *hP*6, *oI*44 and *hp*22, respectively. Available experimental data on the crystallographic data [8–13] of this alloy system and the four pure metals are summarized in Table 1.

All calculations were performed using the Vienna ab initio Simulation Package (VASP) [14,15] based on the density-functional theory (DFT) [16] and the projector augmented plane-wave

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Table 1
Crystallographic data of Ti–Sn alloys considered in this study.

Phase	Pearson symbol	Space group	Prototype
α-Ti [10]	*hP*2	$P6_3/mmc$	Mg
β-Ti [10]	*cI*2	9*m*	W
α-Sn [10]	*cF*8	$Fd\bar{3}M$	C-diamond
β-Sn [10]	*tI*4	$I4_1/amd$	β-Sn
Ti_3Sn [10]	*hP*8	$P6_3/mmc$	Ni_3Sn
Ti_2Sn [10]	*hP*6	$P6_3/mmc$	$InNi_2$
Ti_5Sn_3 [10,11]	*hP*16	$P6_3/mcm$	Mn_5Si_3
α-Ti_6Sn_5 [10,12]	*oI*44	*Immm*	Nb_6Sn_5
β-Ti_6Sn_5 [13]	*hp*22	$P6_3/mmc$	Hexagonal
Ti_2Sn_3 [8,9]	*oS*40	*Cmca*	V_2GaSn_2

(PAW) pseudopotential [17]. The exchange and correlation energy was treated within the generalized gradient approximation of Perdew–Wang 91 version (GGA-PW91) [18]. The electron–ion interaction was described by the pseudopotential with 4 valence electrons (3d and 4s electrons) for Ti, and 14 valence electrons (5s, 5p and semicore 4d electrons) for Sn. The precise testing calculations with a plane-wave cutoff energy of 300 eV have been performed. Brillouin Zone integrations were performed using the Monkhorst–Pack [19] k-point meshes, e.g., the k-point meshes for Ti_3Sn, Ti_2Sn, Ti_5Sn_3, α-Ti_6Sn_5, β-Ti_6Sn_5 and Ti_2Sn_3 were $9 \times 9 \times 11$, $11 \times 11 \times 9$, $7 \times 7 \times 9$, $7 \times 7 \times 7$, $7 \times 7 \times 9$ and $7 \times 7 \times 9$ for the geometry optimization and $19 \times 19 \times 21$, $21 \times 21 \times 19$, $15 \times 15 \times 19$, $13 \times 13 \times 13$, $13 \times 13 \times 19$ and $13 \times 13 \times 15$ for the calculations of density of states (DOS) at the equilibrium volume, respectively. Optimization of the structural parameters (atomic positions and the lattice constants) for each system were performed via a conjugate gradient method, and the coordinates of internal atoms were allowed to relax until the forces on the unconstrained atoms converged to less than 0.01 eV/Å. The total energy and density of states (DOS) calculations were performed with the linear tetrahedron method with Blöchl corrections. All calculations are performed using the "accurate" setting within VASP to avoid wrap-around errors.

3. Results and discussion

3.1. Phase stability and cohesive properties of Ti–Sn alloys

The results of *ab initio* calculations and the experimental data [8,9,13,20–23] for Ti–Sn alloys in Table 2 are plotted in Fig. 1. One can see from Table 2 and Fig. 1 that the equilibrium lattice parameters of Ti–Sn alloys agree with the experimental results within ±1%, except for β-Sn within ±2%. It should be indicated that compared with experimental measurements at ambient temperatures, the present calculations are performed at 0 K, in spite of a very small discrepancy between theoretical and experimental values.

Table 2
A comparison of equilibrium parameters of cell-parameters of Ti–Sn alloys, obtained by *ab initio* calculation and the available experimental data.

Phase	Lattice parameters (Å)	
	Experiment [Ref.]	*ab initio* (This study)
α-Ti	$a = 2.9443$, $c = 4.6685$ [20]	$a = 2.9506$, $c = 4.6788$
β-Sn	$a = 5.812$, $c = 3.157$ [21]	$a = 5.9218$, $c = 3.2285$
Ti_3Sn	$a = 5.916$, $c = 4.764$ [22]	$a = 5.9017$, $c = 4.7395$
Ti_2Sn	$a = 4.653$, $c = 5.69$ [22]	$a = 4.7429$, $c = 5.6219$
Ti_5Sn_3	$a = 8.049(2)$, $c = 5.405(2)$ [22]	$a = 8.0674$, $c = 5.4280$
α-Ti_6Sn_5	$a = 5.69$, $b = 9.22$, $c = 16.1$ [23]	$a = 5.7803$, $b = 9.3664$, $c = 16.3557$
β-Ti_6Sn_5	$a = 9.24$, $c = 5.71$ [13]	$a = 9.2861$, $c = 5.7148$
Ti_2Sn_3	$a = 5.9556(4)$, $b = 19.964(2)$, $c = 7.0281(5)$ [8]; $a = 5.967(4)$, $b = 19.95(2)$, $c = 7.013(4)$ [9]	$a = 6.001$, $b = 20.064$, $c = 7.0425$

The isothermal bulk modulus (B_0) of those structures was estimated by fitting the total energies to the Murnaghan–Birech equation of the states [24]. Fig. 1a shows the variation of B_0 as a function of Sn content. As expected, the change trend of B_0 basically decreases from Ti_3Sn to β-Sn (body-centered tetragonal, bct), i.e., B_0 of Ti_3Sn exhibits the maximum value, B_0 of Ti_2Sn and Ti_5Sn_3 is almost the same, and B_0 of the later three ones (Ti_5Sn_3, Ti_6Sn_5 and Ti_3Sn_2) drops rapidly. It can therefore be concluded from the above result that the Ti_3Sn is more uncompressible than other intermetallics in this system, since bulk modulus determines compressibility. In addition, the calculated B_0 of hcp-Ti and bct-Sn is 115.38 GPa and 57.56 GPa, which is comparable with the experimental values [25,26], respectively.

In order to compare the alloying abilities of the intermetallics in this system, the formation energy (ΔE_F) of per atom of Ti_ASn_B alloys can be calculated by

$$E_{\mathrm{form}}^{\mathrm{Ti}_A\mathrm{Sn}_B} = \frac{1}{A+B}\left[E_{\mathrm{tot}}^{\mathrm{Ti}_A\mathrm{Sn}_B} - A\cdot E_{\mathrm{solid}}^{\mathrm{Ti}} - B\cdot E_{\mathrm{solid}}^{\mathrm{Sn}}\right] \tag{1}$$

where $E_{\mathrm{form}}^{\mathrm{Ti}}$ and $E_{\mathrm{form}}^{\mathrm{Sn}}$ are the energies per atom of pure constituents α-Ti (hexagonal close-packed, hcp) and β-Sn (body-centered tetragonal, bct) in the solid states at equilibrium lattice constant, respectively. Formation energy as a function of Sn content is plotted in Fig. 1b. As seen, all the ΔE_F is negative; note here that a negative value means a strong alloying ability. Furthermore, we find that the convex hull is somewhat asymmetric and moves towards the Ti side rather than the Sn side, unlike the results of Ti–M (M = Zn, Cu) [20,27] described by Ghosh. This difference may be due to the fact that Sn is an element of group IVB and exhibits a larger electronegativity than M (Zn, Cu). The minimum ΔE_F of intermetallics is α-Ti_6Sn_5, indicating the strongest alloying ability for this alloy. In addition, comparing the calculated ΔE_F with the ΔE_F evaluated using Calphal theory [28,29], one can find that both methods predict the same trend. Experimentally, the measured ΔE_F of the α-Ti_6Sn_5 is about $43.4 \pm 1.4\ \mathrm{kJ\ mol^{-1}}$ [30]. The experimental value is a little smaller than the calculated results. This discrepancy may result from the same reason mentioned earlier, i.e., ΔE_F is measured at ambient temperatures while the calculated results are conducted by zero-temperature equations of state. The calculation also shows that ΔE_F of β-Ti_6Sn_5 is lower about $3\ \mathrm{kJ\ mol^{-1}}$ of atom than that of α-Ti_6Sn_5, which seems to be inconsistent with the previous experimental observation that the β phase is more unstable [12]. This happens partly because the entropy differences between the competing polymorphs in the alloy are large enough to reverse their relative stability at the temperatures where experiments have been conducted as described by Ghosh [20].

Fig. 1c shows the calculated cohesive energy, E_C, for all the Ti–Sn intermetallics. It is known that the cohesive energy is the stability of an alloy and a measure of the force to bind atoms together in the solid state. The E_C of per atom of two-component Ti_ASn_B intermetallics can be given by

$$E_{\mathrm{coh}}^{\mathrm{Ti}_A\mathrm{Sn}_B} = \frac{1}{A+B}\left[E_{\mathrm{tot}}^{\mathrm{Ti}_A\mathrm{Sn}_B} - A\cdot E_{\mathrm{atom}}^{\mathrm{Ti}} - B\cdot E_{\mathrm{atom}}^{\mathrm{Sn}}\right] \tag{2}$$

where $E_{\mathrm{atom}}^{\mathrm{Ti}}$ and $E_{\mathrm{atom}}^{\mathrm{Sn}}$ are the energies of the isolated atoms Ti and Sn in the freedom states. Form Fig. 1c, the calculated E_C for all the Ti–Sn alloys increases with decreasing Ti composition and is independent of crystal structure type. It is evident that the intermetallic with the highest Ti composition has the highest stability. Therefore, Ti_3Sn is the most stable in Ti–Sn system, whereas Ti_2Sn_3 is the least stable. Additionally, the mean atomic volume (V_0) for the different Ti–Sn compounds is shown in Fig. 1d. It is interesting