First-principles calculations of structural and elastic properties of $Mg_xTi_{(1\text{-}x)}$ alloys

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In this study, structural, energetics and elastic properties of the $Mg_xTi_{(1\text{-}x)}$ (x=0.125, 0.25, 0.5, 0.75, 0.875) alloys were investigated by means of first-principles calculations within the frame work of density functional theory. The obtained structural parameters were in good agreement with the available experimental values. And the structural stability was also studied from the energetic point of view. The five independent single-crystal elastic constants were calculated, showing that the $Mg_xTi_{(1\text{-}x)}$ alloys were mechanically stable structure. Then the polycrystalline elastic parameters such as bulk modulus B, Young's modulus E, shear modulus G and Poisson's ratio v for $Mg_xTi_{(1\text{-}x)}$ alloys were gained by the Voigt–Reuss–Hill(VRH) approximation. The ductility of $Mg_xTi_{(1\text{-}x)}$ alloys was also analyzed.

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1. Introduction

Tailoring the property of magnesium by forming new alloys or new structures has been the main focus of a number of researches. Mg-Ti alloys are novel metastable state alloys with unique mechanical, optical and hydrogen-storage properties. Several studies have shown that the addition of Ti to magnesium alloys can markedly increase specific strength and stiffness, the corrosion resistance and the capacity of hydrogen storage. However in the reported binary phase diagram of the Mg–Ti system, no intermetallic compound is found and the solubility of each metal to another is less than 2 at.% [1]. It has been known that no alloy between Mg and Ti can be formed through melting preparation methods. Recently, the preparation of Mg–Ti thin films by the sputtering method has been reported [2]. Mg_xTi_{100-x} ($50 \leq x \leq 95$) thin films had the same HCP (hexagonal close packed) structure to Mg and Ti [2]. Liang and Schulz [3] have synthesized Mg_xTi_{100-x} ($x \geq 80$) HCP alloys by means of ball milling. Kalisvaart and Notten [4] have obtained Mg_xTi_{100-x} ($65 \leq x \leq 85$) alloys by means of ball milling which consisted of two face centered cubic (FCC) phases. Asano et al. [5,6] reported $Mg_{50}Ti_{50}$ alloy with a BCC (body centered cubic) structure by means of ball milling. These studies showed that the crystal structure of metastable Mg_xTi_{100-x} alloys depends on the synthesis methods and the ratio of Mg and Ti.

The previous experimental research was mainly focused on crystal structure, thermal stability and hydrogen storage property of Mg_xTi_{100-x} alloys. There however was little theoretical investigation on the elastic property of Mg_xTi_{100-x} alloys. In this work, the lattice constants, formation energy and elastic constants of $Mg_xTi_{(1\text{-}x)}$ (x=0.125, 0.25, 0.5, 0.75, 0.875) alloys were calculated using first-principles calculations within the frame work of density functional theory, and the relations between these structures and elastic constants were investigated.

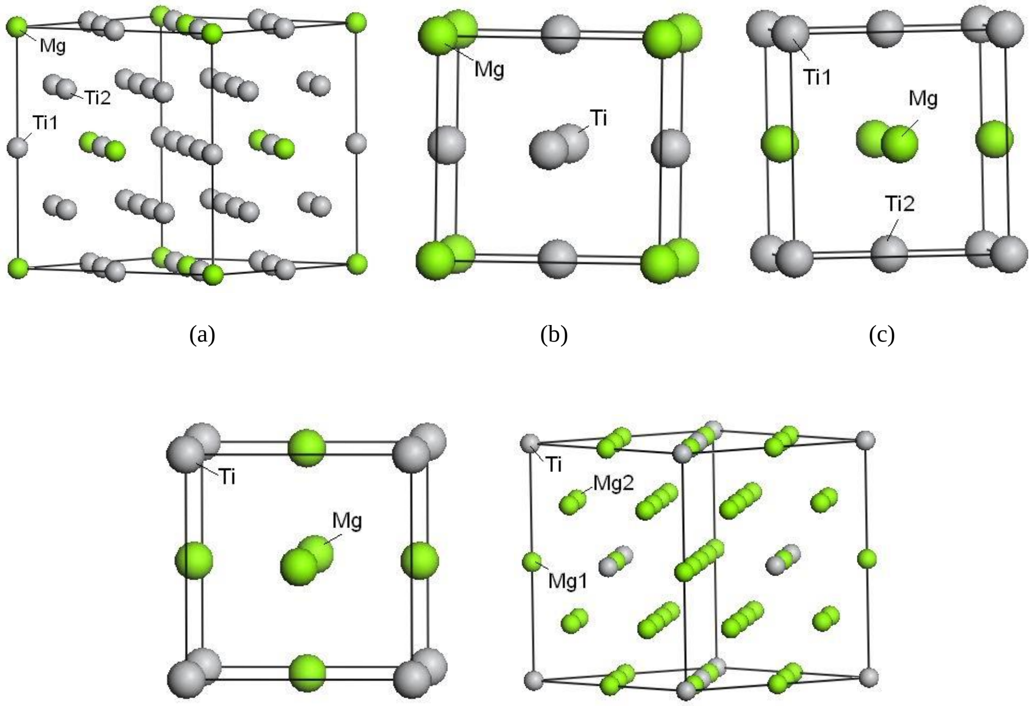
2. Computational method

All calculations were performed using Density Functional Theory (DFT) as implemented in the Quantum-ESPRESSO [7]. The ion–electron interaction was modeled by ultrasoft pseudopotentials [8]. Generalized gradient approximation (GGA) with the PBE exchange-correlation functional [9] was used. The kinetic energy cut-off value for plane-wave expansions was set as 310 eV for all the calculations. The larger values of the cut-off energy of atomic wave functions have been tested, such as 340 eV, 380 eV and 400 eV etc. Tests indicated that the total energies of the crystals have been not obviously decreased. The k-point meshes for Brillouin zone sampling were constructed using Monkhorst–Pack scheme [10] with 16×16×16 grids for $Mg_xTi_{(1\text{-}x)}$ (x=0.125, 0.25, 0.75 and 0.875) alloys, 12×12×16 for $Mg_{0.5}Ti_{0.5}$ alloy. A Gamma centered 18×18×12 mesh was used for hexagonal close-packed metals Mg and Ti. Convergence with respect to the k-point sampling for the Brillouin zone integration was tested independently on the these alloys using regular meshes of increasing density. Tests indicate that the total energy converges to 1 meV/atom. The valence electronic configurations were taken to be $2p^6 3s^2$ for Mg, $3s^2 3p^6 3d^2 4s^2$ for Ti. For all structures the lattice parameters, the volume and the atom positions were allowed to relax simultaneously. The relaxations of cell geometry and atomic positions were carried out using a conjugate gradient algorithm until the Hellman–Feynman force on each of the unconstrained atoms was less than 0.01eV/A°. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 10^{-6} eV at consecutive steps. After the structures are optimized, the total energies are recalculated self-consistently with the tetrahedron method [11].

3. Results and discussion

3.1 Structural properties

The unit cells of $Mg_xTi_{(1-x)}$ (x=0.125, 0.25, 0.5, 0.75 and 0.875) alloys investigated in this study were constructed mainly based on the Ca_7Ge-type, Cu_3Au-type and CuAu-type structural models. For x = 0.125, 0.875 we used the Ca_7Ge structure with the space group $Fm\bar{3}m$ (No.225) to order the metal atoms, for x = 0.25, 0.75 the Cu_3Au ($L1_2$) structure with the space group $Pm\bar{3}m$ (No.221), and for x = 0.5 the CuAu ($L1_0$) structure with the space group P_4/mmm (No.123). Fig. 1 show the structural models of $Mg_xTi_{(1-x)}$ alloys. In each of the structures and compositions the cell parameters were optimized, as well as the positions of all atoms within the cell. The optimized lattice parameters and atomic internal coordinates were shown in Table1. Most of these structures are cubic, except $Mg_{0.5}T_{i0.5}$ which is tetragonally distorted. Kalisvaart et al. [12] reported that the experimental lattice constant of $Mg_{75}Ti_{0.25}$ with FCC structure is 4.40 ⊕ obtained from mechanical alloying method. The equilibrium lattice constants from our calculations are in good agreement with the available experimental value.



(a) (b) (c)

(d) (e)

Fig. 1. Crystal structures of $Mg_xTi_{(1-x)}$ alloys, (a) $Mg_{0.125}Ti_{0.875}$, (b) $Mg_{0..25}Ti_{0.75}$, (c) $Mg_{0..5}Ti_{0..5}$, (d) $Mg_{0.75}Ti_{0.25}$, (e) $Mg_{0.875}Ti_{0.125}$.

Table 1. The optimized equilibrium lattice constants, Wyckoff position, total energies and formation enthalpies of five $Mg_xTi_{(1-x)}$ structures.

Compound	Lattice parameter (⊕)	Wyckoff position	Total energy E_{tot} (eV/ f. u.)	ΔH ($kJ \cdot mol^{-1}$)
$Mg_{0.125}Ti_{0.875}$	8.309	Ti1 4b (1/2, 1/2, 1/2)	-12227.599	-64.13
		Ti2 24d (0, 1/4, 1/4)		
		Mg 4a (0, 0, 0)		
$Mg_{0.25}Ti_{0.75}$	4.174	Ti 3c (0, 1/2, 1/2)	-5799.594	-28.04
		Mg 1a (0, 0, 0)		
$Mg_{0.5}Ti_{0.5}$	a = 4.125	Ti1 1a (0, 0, 0)	-5176.463	-83.62
	c = 4.599	Ti2 1c (1/2, 1/2, 0)		
		Mg 2e (0, 1/2, 1/2)		
$Mg_{0.75}Ti_{0.25}$	4.372	Ti 1a (0, 0, 0)	-4543.417	-19.68
	4.40 [12]	Mg 3c (0, 1/2, 1/2)		
$Mg_{0.875}Ti_{0.125}$	8.969	Ti 4a (0, 0, 0)	-8458.255	-29.26
		Mg1 4b (1/2, 1/2, 1/2)		
		Mg2 24d (0, 1/4, 1/4)		

In order to understand the structural stability of $Mg_xTi_{(1-x)}$ alloys, the formation enthalpy(ΔH) was calculated as follows:

$$\Delta H = (E_{\mathrm{tot}} - N_{\mathrm{Ti}} E_{\mathrm{tot}}(\mathrm{Ti})_{\mathrm{solid}} - N_{\mathrm{Mg}} E_{\mathrm{tot}}(\mathrm{Mg})_{\mathrm{solid}}) / (N_{\mathrm{Ti}} + N_{\mathrm{Mg}}) \quad (1)$$

where E_{tot} is the total energy of $Mg_xTi_{(1-x)}$ cell unit; $E_{\mathrm{tot}}(\mathrm{Mg})_{\mathrm{solid}}$ and $E_{\mathrm{tot}}(\mathrm{Ti})_{\mathrm{solid}}$ are the total energy of per atom of pure solid states Mg and Ti, respectively; N_{Ti} and N_{Mg} refer to the numbers of Ti and Mg atoms in unit cell of $Mg_xTi_{(1-x)}$, repectively. The calculated negative formation enthalpies in Table 1 indicated that $Mg_xTi_{(1-x)}$ alloys are stable from energetic point of view, and $Mg_{0.5}Ti_{0.5}$ has the highest structural stability, and then followed by $Mg_{0.125}Ti_{0.875}$, $Mg_{0.875}Ti_{0.125}$ and $Mg_{0.25}Ti_{0.75}$.

3.2 Elastic constants and the anisotropy factor

The elastic constants of solids are very important because they are closely associated with the mechanical and physical properties. In particular, they play an important part in providing valuable information about structural stability and anisotropic characteristics. For cubic symmetry crystal structure of $Mg_xTi_{(1-x)}$ (x=0.125, 0.25, 0.75 and 0.875) alloys, there are three independent elastic constants (C_{11}, C_{12} and C_{44}). For the tetragonal symmetry of $Mg_{0.5}Ti_{0.5}$ alloy, there are six independent elastic constants (C_{11}, C_{12}, C_{12}, C_{33}, C_{44} and C_{66}). The formulas for the calculations of elastic constants were described in details in Ref.[13]. The calculated values of the elastic constants $C_{i\,j}$ are shown in Table 2. To our knowledge, there have been no experimental and theoretical values of the elastic constants on single crystal $Mg_xTi_{(1-x)}$ in literatures. Future experimental measurements will validate our calculated results. The shear anisotropic factor (A) was calculated for the cubic crystal structures using the following relation [14].

$$A = 2C_{44} / (C_{11} - C_{12}) \quad (2)$$

The calculated shear anisotropic factors of $Mg_xTi_{(1-x)}$ alloys with the cubic phase are given in Table 2. For an isotropic crystal, A is equal to 1, while any value smaller or larger than 1 indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. The deviation from 1 is larger for all the $Mg_xTi_{(1-x)}$ alloys studied here.

Table 2. The calculated elastic constants, C_{ij} (in GPa) for $Mg_xTi_{(1-x)}$ alloys.

Material	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	A
$Mg_{0.125}Ti_{0.875}$	117.47	66.14	-	-	44.82	-	1.75
$Mg_{0.25}Ti_{0.75}$	126.82	56.34	-	-	44.93	-	1.25
$Mg_{0.5}Ti_{0.5}$	85.15	44.83	49.12	82.65	59.95	-5.22	-
$Mg_{0.75}Ti_{0.25}$	48.85	47.59	-	-	47.44	-	75.3
$Mg_{0.875}Ti_{0.125}$	40.40	29.89	-	-	31.77	-	6.05

3.3 Elastic properties for polycrystalline materials

The elastic stability is a necessary condition for a solid to exist. The intrinsic mechanical stability of a solid is in general determined by certain conditions related to the crystal symmetry [15] and the following criteria based on relations between elastic constants have to be fulfilled.

For cubic phases,

$$C_{11} > \left|C_{12}\right|,\ C_{11} + 2C_{12} > 0 \text{ and } C_{44} > 0 \qquad (3)$$

For tetragonal phases,

$$C_{11} + C_{33} - 2C_{13} > 0,\ 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0$$

$$\text{and } (2C_{11} + C_{33})/3 - B > 0 \qquad (4)$$

As shown in Table 2, all the elastic constants of $Mg_xTi_{(1-x)}$ alloys satisfy the above restrictions, so all these structures are mechanically stable.

To account for a polycrystalline material, the upper and lower bounds (Reuss and Voigt [13]) of bulk (B_R, B_V) and shear (G_R, G_V) moduli are found from single crystal elastic constants. Subsequently, a simple average of those bound values of B_R, B_V and G_R, G_V is calculated as proposed by Hill [16]. For the detailed description of this issue concerning the polycrystalline materials see [17] and references therein. Further on, we refer to Hill's averaged values of bulk and shear modulus (B, G) that are used for evaluation of quantities describing polycrystalline material [17] such as Pugh ratio (B/G), Poisson's ratio ($\gamma = (3B - 2G)/(6B + 2G)$), Young's modulus ($E = 9BG/(3B + G)$) of all $Mg_xTi_{(1-x)}$ alloys studied which are summarized in Table 3. Note that the difference between B_V and B_R is comparatively small. As seen from Table 3, the calculated bulk modulus of $Mg_xTi_{(1-x)}$ alloys increases with increase of Ti content in Mg-Ti alloys, indicating that the resistance to volume change by applied pressure is eventually improved. The shear modulus, G and Young's modulus, E of $Mg_xTi_{(1-x)}$ alloys however exhibit the different trend. A predicted feature is that the resistance to reversible deformations upon shear stress and the stiffness decrease rapidly for $Mg_xTi_{(1-x)}$ ($x>0.5$) alloys. The results in Table 3 also suggest that the Young's modulus of $Mg_{0.25}Ti_{0.75}$ is highest, indicating that it is the stiffest, while $Mg_{0.75}Ti_{0.25}$ is the most flexible.

Table 3. The calculated bulk moduli (in GPa), B_V, B_R and $B = (B_R+B_V)/2$, shear moduli (in GPa), G_R, G_V and $G = (G_R+G_V)/2$, Young's modulus (in GPa), E, and Poisson's ratio, γ, for $Mg_xTi_{(1-x)}$ alloys.

Material	B_V	B_R	B	G_V	G_R	G	E	B/G	γ
$Mg_{0.125}Ti_{0.875}$	83.25	83.24	83.24	37.16	34.52	35.84	69.83	2.32	0.36
$Mg_{0.25}Ti_{0.75}$	79.83	79.83	79.83	41.05	40.48	40.76	92.16	1.96	0.31
$Mg_{0.5}Ti_{0.5}$	59.90	59.90	59.90	30.26	-104.84	-37.29	51.58	-1.60	0.28
$Mg_{0.75}Ti_{0.25}$	48.02	48.02	48.02	28.72	1.54	15.13	1.87	2.70	0.49
$Mg_{0.875}Ti_{0.125}$	33.39	33.39	33.39	21.16	10.53	15.84	14.98	2.11	0.43

The ratio of the bulk modulus to shear modulus of crystalline phases, proposed by Pugh [18], can empirically predict the brittle and ductile behavior of materials. A high B/G ratio is associated with ductility, whereas a low value corresponds to brittle nature. The critical value which separates ductile and brittle material is around 1.75. In the case of the cubic $Mg_xTi_{(1-x)}$ (x=0.125, 0.25, 0.75, 0.875) structures, our calculated values of B/G are higher than 1.75, hence describing the structure of these materials as ductile. While the values of $Mg_{0.5}Ti_{0.5}$ alloy is lower than 1.75, which means that this structure is brittle. Generally, metals with a Poisson's ratio around 1/3 are ductile, where as metals having a Poisson's ratio less than 1/3 are inferred as being brittle. The ductility and brittleness of the $Mg_xTi_{(1-x)}$ (x=0.125, 0.25, 0.5, 0.75, 0.875) based on Poisson's ratio γ criterion are in good agreement with the results estimated by the B/G ratio except for $Mg_{0.25}Ti_{0.75}$, as shown in Table 3.

A lower Young's modulus E and G and higher Poisson's ratio γ in case of $Mg_{0.75}Ti_{0.25}$ and $Mg_{0.875}Ti_{0.125}$ alloys correlate with weaker and less directional interatomic bonding, and hence with an increase of ductile behavior. This is again in accord with trends preceding Pugh criteria.

4. Conclusions

The enthalpies of formation, crystal structures and elastic properties of $Mg_xTi_{(1-x)}$ (x=0.125, 0.25, 0.5, 0.75, 0.875) alloys were predicted by means of first-principles calculations. All five structural models are stable from the thermodynamic point of view and are also mechanically stable considering mechanical stability conditions based on single elastic constants. We have also calculated the bulk moduli, B; the shear modulus, G; Young's modulus, E; and Poisson's ratio, γ; for polycrystalline $Mg_xTi_{(1-x)}$ alloys. The results show that bulk modulus of $Mg_xTi_{(1-x)}$ alloys increases with increase of Ti content. The shear modulus, G and Young's modulus, E of $Mg_xTi_{(1-x)}$ alloys however exhibit the different trend. $Mg_{0.75}Ti_{0.25}$ alloy possesses the lowest shear, Young's modulus and the highest Poisson's ratio of the five alloys, indicating that the structure of this material is most ductile.

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