INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 1888–1896

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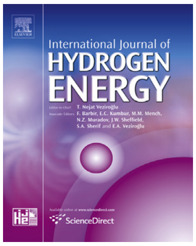

Effect of hydrogen concentration on various properties of gamma TiAl

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ARTICLE INFO

Article history:
Received 16 September 2013
Received in revised form
5 November 2013
Accepted 12 November 2013
Available online 15 December 2013

Keywords:
TiAl and TiAlH
Phase stability
Elastic property
Thermodynamic property
First principles calculation

ABSTRACT

First principles calculation reveals that the TiAlH phases become relatively less stable after the addition of more H atoms, and that the H migration from tetrahedral interstitial site to octahedral site in gamma TiAl should be much easier than that between octahedral sites. Calculation also shows that H concentration has an important effect on mechanical properties of TiAlH phases, and that the energetically favorable TiAlH phase should possess bigger *E*, *G*, and *G*/*B* values as well as lower elastic anisotropy. Moreover, it is found that the heat capacities of TiAlH phases increase with the increase of H concentration, and that the coefficients of thermal expansion of TiAl and TiAlH phases decrease with the increase of pressure.

1. Introduction

During the past decades, the interaction between hydrogen (H) and gamma TiAl phase has induced considerable interests among researchers [1–7]. On the one hand, with high specific strength, good oxidation resistance at high temperature, and low density, gamma TiAl is widely considered as promising high-temperature structural materials such as aerospace, marine and automotive engine components [8–13], etc., which are apt to hydrogen attack or have close contacts with the fuel of H_2 [14,15]. On the other hand, gamma TiAl is commonly regarded as a kind of promising materials for hydrogen storage, as it has a light weight and possesses a hydride forming element of Ti and a non-hydride forming element of Al, which are beneficial for both hydrogenation and dehydrogenation [16]. Furthermore, the gamma TiAl with the porous structure could be utilized as a potential support of Pd membranes for the purpose of hydrogen separation and purification [17].

Regarding various properties of TiAlH phases, there are already a lot of investigations in the literature [1–7,16,18–24]. For instance, several experimental techniques were performed to find out diffusion coefficients of H [1,2], hydride formation [1,3,4,19], H adsorption and desorption [1,3,4,16,20], as well as effects of H on mechanical properties of TiAl [5–7,18–20], etc. Very recently, first principles calculation was conducted to reveal the effect of Al composition on structural stability, mechanical properties, elastic anisotropy, and electronic structures of various TiAl phases with a low H composition [24]. Unfortunately, it should be pointed out that there is no any study regarding the effect of H composition on structural stability and thermodynamic properties of gamma TiAl in the literature.

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http://dx.doi.org/10.1016/j.ijhydene.2013.11.045

By means of highly accurate total energy calculations based on density function theory, the present study is therefore dedicated to have a systematic investigation of structural, mechanical, and thermodynamic properties of gamma TiAl phases as a function of H composition. The derived results will be compared with experimental evidence in the literature and the fundamental mechanism will be revealed through discussion, which could not only provide useful guidance for experimentalists, but also give a deep understanding of the underlying relationship between the structure and property of TiAlH phases.

2. Calculation method

The present first principles calculation is based on the well-established Vienna *ab initio* simulation package (VASP) within the density functional theory [25]. The interactions between electrons and ions are described by the projector-augmented wave (PAW) method [26]. The exchange and correlation items are treated by generalized gradient approximation (GGA) of Perdew et al. [27] and the cutoff energies are 400 eV for plane-wave basis and augmentation charge. For the Brillouin zone sampling, the temperature smearing method of Methfessel-Paxton [28] is used for dynamical calculation and the modified tetrahedron method of Blöchl-Jepsen-Andersen [29] is performed for static calculation.

In the present study, six H concentrations are chosen, i.e., Ti_1Al_1H, Ti_2Al_2H, Ti_4Al_4H, Ti_8Al_8H, $Ti_{16}Al_{16}H$, and pure TiAl phases with the supercell models of 2, 4, 8, 16, 32, and 4 metal atoms, respectively. At each concentration, the ordered $L1_0$ (space group P4/mmm) is selected, and only one H atom is added at the octahedral (O) and tetrahedral (T) interstitial sites of each phase, respectively. It should be noted that for each phase, there is only one T site, while two O sites, i.e., the site surrounded by four Ti and two Al atoms is named O1, and the other by four Al and two Ti atoms is called O2. For simplicity, the H locations are symbolized by Ti_mAl_mH(O1), Ti_mAl_mH(O2), and Ti_mAl_mH(T) in the following text, tables, and figures, e.g., Ti_4Al_4H(O1) signifies the Ti_4Al_4H phase with H at the O1 site.

After the test calculation, for Ti_1Al_1H, Ti_2Al_2H, Ti_4Al_4H, Ti_8Al_8H, $Ti_{16}Al_{16}H$, and TiAl phases, the *k*-meshes of 21 × 21 × 13, 13 × 13 × 13, 13 × 13 × 7, 7 × 7 × 13, 7 × 7 × 7, and 13 × 13 × 13 are adopted for relaxation calculations, while 25 × 25 × 17, 17 × 17 × 17, 17 × 17 × 9, 9 × 9 × 17, 9 × 9 × 9, and 17 × 17 × 17 for static calculations, respectively. In each calculation, periodic boundary conditions are added in three directions, and the unit cell is allowed to fully relax. The energy criteria are 0.1 and 0.01 meV for ionic and electronic relaxations, respectively, while 0.001 meV for static calculation.

3. Results and discussion

3.1. *Phase stability*

After a series of calculations, the lattice constants of gamma TiAl and various Ti_mAl_mH phases are derived and summarized in Table 1. For comparison, the experimental and calculated lattice constants of TiAl in the literature [30–34] are also listed in Table 1. It can be seen that the present lattice constants *a*, *c*, and *c*/*a* of gamma TiAl are 3.990 Å, 4.073 Å, and 1.02, respectively, which match well with the corresponding experimental data ($a = 3.99$ or 3.997 Å; $c = 4.07$ or 4.077 Å; $c/a = 1.02$) [30,31]. In addition, it could be also deduced from Table 1 that both lattice constant *c* of O1 site and lattice constant *a* of O2 site increase with the increase of H concentration. Considering that there are two Al atoms in the *c* direction of O1 site as well as four Al atoms in the *a* directions of O2 site, the above increases of lattice constants imply that the interaction between Al and H atoms should be mainly repulsive, and the present statement would be compatible with the experimental observation that the absorption of hydrogen in TiAl decreases with the increase of Al composition [16].

To find out phase stability, the heats of formation (ΔH_f) of TiAl and Ti_mAl_mH phases, are calculated by means of the following formulas, respectively:

$$\Delta H_f = \frac{E_{TiAl} - 2(E_{Ti} + E_{Al})}{4}, \tag{1}$$

$$\Delta H_f = \frac{E_{Ti_mAl_mH} - \left(mE_{TiAl} + \frac{1}{2}E_{H_2}\right)}{2m+1}, \tag{2}$$

where E_{TiAl}, E_{Ti}, E_{Al}, $E_{Ti_mAl_mH}$, and E_{H_2} are total energies of TiAl, HCP Ti atom, FCC Al atom, Ti_mAl_mH, and H_2 molecule, respectively. As a result, Table 1 lists the derived ΔH_f values of TiAl and various Ti_mAl_mH phases as well as corresponding ΔH_f values of TiAl in the literature [33,35]. Moreover, Fig. 1 shows the comparison of ΔH_f values of Ti_mAl_mH(O1), Ti_mAl_mH(O2), and Ti_mAl_mH(T) phases as a function of H concentration.

Several features could be observed from Fig. 1 as well as Table 1. Firstly, one sees from Table 1 that the present ΔH_f value of the gamma TiAl phases with the $L1_0$ structure is calculated to be −39.368 kJ/mol, which agrees well with the corresponding experimental value of −37.6 kJ/mol [35]. This

Table 1 – Lattice constants (*a* and *c*) and heats of formation (ΔH_f) of TiAl and Ti_mAl_mH phases with the $L1_0$ structure.

Phase	Type	*a* (Å)	*c* (Å)	*c*/*a*	ΔH_f (kJ/mol H)
TiAl	This work	3.990	4.073	1.02	−39.368
	Exp.	3.997 [30]	4.077 [30]	1.02	−37.6 [35]
	Exp. [31]	3.99	4.07	1.02	
	Cal. [32]	3.96	4.08	1.03	
	Cal. [33]	3.995	4.075	1.02	−39.2
	Cal. [34]	3.97	4.05	1.02	
$Ti_{16}Al_{16}H$(O1)	This work	3.990	4.085	1.024	−0.28
$Ti_{16}Al_{16}H$(O2)	This work	4.000	4.070	1.018	1.05
$Ti_{16}Al_{16}H$(T)	This work	3.999	4.083	1.021	0.56
Ti_8Al_8H(O1)	This work	3.989	4.098	1.027	−0.26
Ti_8Al_8H(O2)	This work	4.011	4.057	1.011	2.61
Ti_8Al_8H(T)	This work	4.011	4.085	1.018	1.14
Ti_4Al_4H(O1)	This work	3.995	4.107	1.028	−0.82
Ti_4Al_4H(O2)	This work	4.050	4.020	0.993	4.61
Ti_4Al_4H(T)	This work	4.028	4.101	1.018	1.77
Ti_2Al_2H(O1)	This work	3.991	4.163	1.043	0.004
Ti_2Al_2H(O2)	This work	4.099	3.969	0.968	6.76
Ti_2Al_2H(T)	This work	4.073	4.114	1.010	4.03
Ti_1Al_1H(O1)	This work	3.967	4.333	1.092	0.65
Ti_1Al_1H(O2)	This work	4.194	3.878	0.925	7.18
Ti_1Al_1H(T)	This work	4.141	4.175	1.008	5.45