Interplay between effect of Mo and chemical disorder on the stability of β/β_o-TiAl phase

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ABSTRACT

The effect of Mo and chemical disorder on chemical, mechanical and dynamical phase stability of β(bcc)/ β_o (B2)-TiAl is studied using Density Functional Theory. The ordered β_o structure has more negative energy of formation, hence it is chemically more stable than the disordered β structure. Our calculations further suggest that the ordered structure is mechanically unstable for Mo concentrations $\lesssim$ 4 at.%. Surprisingly, the disordered β phase is found to be mechanically stable regardless the Mo content. It is therefore concluded that the chemical disorder and the Mo alloying play a similar role in the stabilisation of β/β_o-TiAl. This trend is further confirmed by studying phonon and electronic density of states. Finally, the ordered β_o structure is shown to sit in a saddle point of a potential energy surface. A barrier-less transformation path $\beta_o \rightarrow \gamma$ exists, allowing for a spontaneous transformation from the symmetry stabilised β_o to the ground state γ-phase.

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1. Introduction

Titanium aluminides (TiAl) represent a novel class of lightweight intermetallic alloys with good oxidation resistance as well as specific strength and creep properties [1,2]. The two major constituents of the microstructure at room temperature (RT) are a tetragonal face-centred γ (TiAl) phase (L1$_0$, space group $P4/mmm$) and a hexagonal α_2 (Ti$_3$ Al) phase (D0$_{19}$, space group $P6_3/mmc$) [3]. Unfortunately, these phases suffer from low ductility, even at high temperatures where hot-forming is conducted at technical deformation rates [1,3]. To overcome this shortcoming and hence to increase the hot-workability of the γ-TiAl-based alloys to be industrially machinable, alloys containing also a cubic β_o (TiAl) phase (B2, space group $Pm\overline{3}m$) at RT have been developed [1]. This phase does not appear in the equilibrium phase diagram of the binary Ti–Al system [4], but can be stabilised by alloying with Nb or Mo [5,6].

More specifically, the body centred cubic phase has two variants: disordered high-temperature, usually labelled as β (A2, space group $Im\overline{3}m$), and the low temperature ordered β_o phase. The ordered CsCl-type structure possess two sublattices which in the case of stoichiometric TiAl are one fully occupied with Al while the other one with Ti atoms. On the other hand, the two sublattices are randomly occupied with both species in the disordered β phase.

Depending on the exact chemical composition, the alloy passes through different phase fields upon its cooling, and hence various temperature dependent phase fractions can be obtained. The specific role of the disordered β phase stems from the fact that it provides a sufficient number of independent slip systems. Consequently, high-temperature workability is significantly improved. On the other hand, the phase fraction of the ordered β_o phase should be minimised at service temperature not to deteriorate the creep behaviour as reported for various β-phase containing TiAl alloys in Refs. [1,7–9]. Further information on engineering β-stabilised TiAl alloys, e.g. composition, microstructure, technology, and applications, can be found in a recent review article [1]. It is therefore of immense interest to understand the impact of the β-stabilising elements on phase stability and ordering phenomena in TiAl. In this work, we theoretically investigate the effect of Mo on the stability and mechanical properties of β/β_o-TiAl by means of first principles calculations.

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2. Methods

Density Functional Theory [10,11] calculations were performed using Vienna Ab initio Simulation Package [12,13]. Projector augmented-wave method-based pseudopotentials [14] were used to describe the ion–electron interactions within the generalised gradient approximation [15]. The plane-wave cut-off energy of 600 eV and more than 8000k-points $\times$ atom guarantee total energies to be converged to less than 1 meV/at. For each structure we optimised its volume and relaxed the internal atomic coordinates using the conjugate–gradient scheme. The electronic states occupancies were smeared using the Methfessel–Paxton scheme [16] with $\sigma = 0.2$ eV.

There exists some controversy on occupancy site preference for Mo in TiAl. Jinlong et al. [17] showed that Mo has no preference in stoichiometric γ-TiAl, and it prefers Ti(Al) site for Al-rich(poor) compositions. The same result has been reported also by Jiang [18]. On the other hand, Song et al. [19] claimed that Mo prefers the Ti sublattice. However, the latter report does not specify for which phase their conclusions hold. Since the focus of this work is on Al-poor compositions, i.e., Ti$_{0.5}$ Al$_{0.5-x}$ Mo$_x$, we assumed the former scenario in which substitutionally alloyed Mo atoms sit on the Al sublattice in the β_o phase. This is also supported by our calculations of the site preference in β-TiAl employing the site preference energy, E_s defined as [20,21]:

$$E_s = E_{Ti_{n-1}MoAl_n} - E_{Ti_nMoAl_{n-1}} - E_{Al} + E_{Ti}. \qquad (1)$$

Here, $E_{Ti_{n-1}MoAl_n}$ and $E_{Ti_nMoAl_{n-1}}$ are total energies of structures with one Ti and Al atom, respectively, replaced with one Mo atom, and E_{Al} and E_{Ti} are total energies of Al and Ti atom, respectively, in their stable crystal structure (fcc and hcp). Eq. (1) yields $E_s = 1.41$ eV for the β_o-TiAl (preferential occupation of the Al sublattice), while $E_s = -0.48$ eV for the γ phase (preferential occupation of the Ti sublattice, in agreement with e.g. Ref. [20]).

The chemical disorder was modelled using Special Quasi-random Structures (SQSs) [22,23] using $3 \times 3 \times 3$ supercells (54 atoms in total). Mo additions were introduced in two different ways: ordered (β_o) structures have one sublattice fully populated by Ti, while Al and Mo mix on the other sublattice (thus resulting in a quasi-binary solid solution of TiAl and TiMo). On the contrary, in the disordered (β) cells, Al, Ti and Mo atoms occupy all bcc lattice sites according to the SQS approach. In this work we focus mostly on a maximum Mo content of ≈ 8 at.%, hence replacing up to 4 Al atoms with Mo as the 54-atom supercells allow for compositional steps of 1.85 at.%.

Elastic constants were calculated using a stress–strain method employing a set of linearly independent strains [24]. Since chemical disorder and/or alloying Mo destroy the macroscopic cubic symmetry, a projection technique to restore the desired symmetry of the tensor of elastic constants was used [25,26]. Subsequently, we used the Reuss-Voight-Hill approach to estimate elastic constants corresponding to an isotropic polycrystalline aggregate [27]. Phonon calculations on selected structures were performed using the finite displacement harmonic approximation as implemented in the Phonopy code [28].

3. Results

3.1. Structural impact of Mo on β/β_o-TiAl

Replacing Al by Mo results in slightly decreasing lattice parameter (Fig. 1). However, the scatter of the data due to the finite cell-size effects are larger than overall decrease, and hence the linear trend lines in Fig. 1 should not be over-interpreted.

Nevertheless, there is a clear distinction between the ordered and disordered structures, the latter having lattice parameter by ≈ 0.02 Å larger. In the case of disordered structures we have also used a smaller $2 \times 2 \times 2$ supercell, in which one Al atom replaced by one Mo atom corresponds with overall Mo content of 6.25 at.%. The lattice parameter of this SQS lies in the same range as the data-points from larger supercells, hence suggesting that the supercell-size effects should not be an issue for the following discussion.

Energy of formation, E_f, expresses the energy gain upon forming a compound or an alloy from the individual components in their respective crystalline form:

$$E_f = E(Ti_{0.5}Al_xMo_{0.5-x}) - [0.5E_{Ti} + xE_{Al} + (0.5 - x)E_{Mo}]. \qquad (2)$$

As shown in Fig. 2, $E_f < 0$ for all compositions and for both β_o and β structures, thus suggesting that both ordered and disordered structures are chemically stable. Energy of formation of the β phase slightly increases with Mo content (i.e. Mo chemically destabilises the β phase), while strong decrease of E_f with Mo content increase in the ordered phase is predicted. Additionally, the ordered phase exhibits lower energy of formation than the disordered one for every composition. This is in agreement with the experimental TiAl–Mo phase diagram showing that, when stable, the β_o phase is stable below the ordering temperature of ≈ 1265 °C [29].

The shaded areas in Fig. 2 show mixing enthalpy, H_{mix}, an energy gain of the ternary alloy with respect to the binary boundary system TiAl and TiMo:

$$H_{mix} = E(Ti_{0.5}Al_xMo_{0.5-x}) - [xE(Ti_{0.5}Al_{0.5}) \\ + (1 - x)E(Ti_{0.5}Mo_{0.5})]. \qquad (3)$$

All quantities on the right hand side of the above equation are total energies per atom. Positive values of H_{mix} in the case of disordered alloy suggest existence of de-mixing forces towards phase separation. These are, however, much smaller than the ordering driving force (difference between E_f of β_o and β). The ordered phase is stable with respect to the boundary β_o-TiAl and β_o-TiMo systems in the whole investigated compositional range.
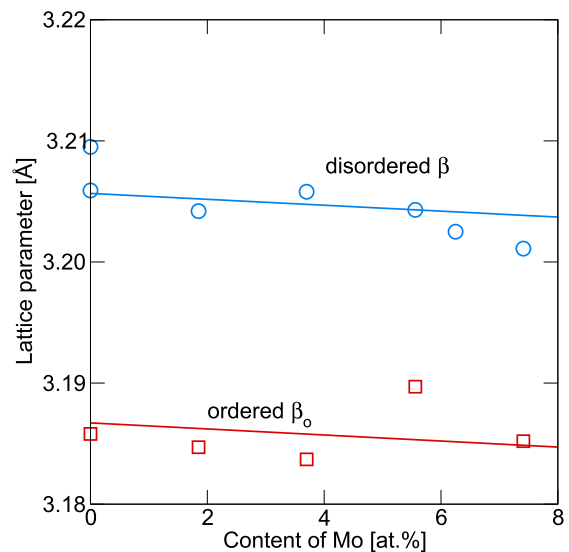

Fig. 1. Calculated lattice constants of ordered (β_o) and disordered (β) Ti$_{0.5}$ Al$_{0.5-x}$ Mo$_x$ alloys.