Vacancy-induced brittle to ductile transition of W-M co-doped Al$_3$Ti (M=Si, Ge, Sn and Pb)

Mingke Zhu$^{1,2}$, Ping Wu$^3$, Qiulin Li$^2$ & Ben Xu$^1$

We investigated the effect of vacancy formation on brittle (D0$_{22}$) to ductile (L1$_{2}$-like) transition in Al$_3$Ti using DFT calculations. The well-known pseudogap on the density of states of Al$_3$Ti migrates towards its Fermi level from far above, via a W – M co-doping strategy, where M is Si, Ge, Sn or Pb respectively. In particular, by a W – M co-doping the underline electronic structure of the pseudogap approaches an octahedral (L1$_{2}$: t$_{2g}$, e$_g$) from the tetragonal (D0$_{22}$: e$_g$, b$_{2g}$, a$_{1g}$, b$_{3g}$) crystal field. Our calculations demonstrated that (1) a W-doping is responsible for the close up of the energy gap between a$_{1g}$ and b$_{2g}$ so that they tend to merge into an e$_g$ symmetry, and (2) all M-doping lead to a narrower gap between e$_g$ and b$_{2g}$ (moving towards a t$_{2g}$ symmetry). Thus, a brittle to ductile transition in Al$_3$Ti is possible by adopting this W – M co-doping strategy. We further recommend the use of W-Pb co-doped Al$_3$Ti to replace the less anodic Al electrode in Al-battery, due to its improved ductility and high Al diffusivity. Finally this study opens a new field in physics to tailor mechanical properties by manipulating electron energy level(s) towards higher symmetry via vacancy optimization.

Brittle to ductile transition is of interest to a wide range of fundamental research and applications$^{1-6}$. In particular, effects of either intrinsic vacancy$^{7,8}$, extra-electron$^9$, or dopants$^{10,11}$ on brittle-ductile transition in Nb$_5$Si$_3$, NiSc, Al$_{12}$W-type and L1$_2$-Al$_5$Sc are reported. TiAl-based intermetallic compounds are desirable candidates for high temperature structural applications due to many attractive properties. Among the Al-Ti alloys, Al$_3$Ti has received particular interests for its high specific strength, elastic moduli$^{13}$, low density (~3.3 g/cm$^3$), good thermal conductivity and high melting point (~1400°C). However, the stable but brittle tetragonal D0$_{22}$-Al$_3$Ti is less favored in real applications. Many investigations are conducted aiming to improve the ductility of D0$_{22}$-Al$_3$Ti. Hong$^{12}$ calculated the density of states (DOS) of the brittle D0$_{22}$-Al$_3$Ti and the ductile L1$_2$-Al$_3$Ti phases, and proposed a strategy to simultaneously stabilize the ductile L1$_2$ and destabilized the brittle D0$_{22}$ phase by ternary alloy additions. He further pointed out that by adding in lower-valence elements, the pseudogap (on DOS) migrates from above to below the Fermi level, thus, diminishing simultaneously the antibonding for the ductile L1$_2$ and the bonding states for the brittle D0$_{22}$ phases. But Hong did not take into consideration the formation of either intrinsic or extrinsic defects into his model. On the other hand, Niu$^7$ proposed to promote ductile to brittle transitions in Al$_3$W-type intermetallic by an extra-electron doping, which is on the opposite direction of the current work. The underline electronic structures of pseudogap in both D0$_{22}$ and L1$_2$-Al$_3$Ti phases are reported recently by Chen$^{14}$. Crystal field splitting as shown in Fig. 1 is found responsible for the formation of the pseudogaps, i.e., an octahedral crystal field of e$_g$ (d$_{x^2−y^2}$, d$_z^2$) and t$_{2g}$ (d$_{xy}$, d$_{yz}$, d$_{zx}$) for the ductile L1$_2$ phase, and a tetragonal one of b$_{2g}$ (d$_{x^2−y^2}$), a$_{1g}$ (d$_z^2$), b$_{3g}$ (d$_{xy}$) and e$_g$ (d$_{xy}$, d$_{yz}$) for the brittle D0$_{22}$ phase. It is interesting to notice that the main difference between the octahedral and tetragonal crystal field splitting is the elongation in tetragonal along the z-axis, which relaxes the electron density along the z-axis and moves (1) the d$_z^2$ energy downwards apart from the d$_{x^2−y^2}$ and (2) the d$_{xy}$ and d$_{yz}$ lower than the d$_{x^2−y^2}$ level. An effective unit area as shown in Fig. 2a is defined as S = l$_x$ × l$_y$, where l$_x$ and l$_y$ is respectively the shortest atomic distance along the x and y axis. By shrinking the unit cell (or d in Fig. 2a) along the z-axis or expanding in the xy-plane indicated by S, a tetragonal crystal structure may return to an octahedral-like structure. Thus, by reducing the ratio r (Å$^{-1}$) (r = d/S), a brittle-ductile transition may be facilitated. From first-principles calculations, we test this new strategy to achieve the designed reduction of r by adopting a W – M co-doping strategy. Key challenges in this approach are (1) to generate sufficient Al

---

$^1$School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, P. R. China. $^2$Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, P. R. China. $^3$Singapore University of Technology and Design, 487372, Singapore, Singapore. Correspondence and requests for materials should be addressed to P.W. (email: wuping@sutd.edu.sg) or Q.L. (email: liql@sz.tsinghua.edu.cn)
vacancies in D0$_{22}$-Al$_3$Ti to make the brittle structure more deformable and (2) to manipulate specific electron energy levels to transfer the low symmetry tetragonal to a high symmetry octahedral-like crystal field. Moreover, due to the decrease in Gibbs free energy, Al$_3$Ti may also be used as the anode material to replace Al in Al-battery. Recently, electronic structure of pure D0$_{22}$-Al$_3$Ti and Al diffusion mechanisms of D0$_{22}$-Al$_3$Sc are reported. However, like many brittle intermetallics, short cycling life of a native D0$_{22}$-Al$_3$Ti electrode is expected due to the structure damages during the charge and discharge processes. In addition, high Al diffusivity is essential to Al-battery, which requires an easy formation of Al vacancy based on Shi’s findings that Al vacancies facilitate the Al diffusion in Al$_3$Sc. Therefore, the current study on the formation of Al vacancies may provide practical solutions to enhance both the mechanical and electrochemical properties of Al$_3$Ti for Al-battery applications.

**Results**

**Crystal structure.** Crystal structures of both the ductile (L1$_2$) and brittle (D0$_{22}$) phases are shown in the Fig. 1. A L1$_2$-Al$_3$Ti crystallizes in the $Pm \bar{3} m$ space group, in which the Al atoms are located at the face centers of the cubic lattice and the Ti atoms are located at the vertices. And a D0$_{22}$-Al$_3$Ti crystallizes in the $I4/mmm$. The conventional D0$_{22}$ cell contains two Al atoms at the Wyckoff site 2a (defined as Al$_1$), four Al atoms at the 4d site (defined as Al$_2$) and two Ti atoms at the 2a site. In this study, the lattice parameters are fixed at the values of

**Figure 1.** Comparison of the lattice and electronic structures between D0$_{22}$-Al$_3$Ti and L1$_2$-Al$_3$Ti. The schematic diagram between the two structures shows that for the tetragonal D0$_{22}$-Al$_3$Ti, the 3d-orbital splits into $b_{1g}$ ($d^2_{x^2-y^2}$), $a_{1g}$ ($d^2_z$), $b_{2g}$ ($d_{xy}$) and $e_g$ ($d_{x^2-y^2}$ $d_{xy}$), while for the octahedral L1$_2$-Al$_3$Ti, the 3d-orbital splits into $e_g$ ($d^2_{x^2-y^2}$ $d^2_z$) and $t_{2g}$ ($d_{xy}$ $d_{xz}$ $d_{yz}$).

**Figure 2.** (a) Crystal structure of the W – M co-doping Al$_3$Ti (Note that the unit cell length (d) along the z-axis and the effective unit area (S) are highlighted, where $l_x$ is the length between M and Ti and $l_y$ is the length between Al and W). (b) The calculated ratio $r$ (Å$^{-1}$) ($r = d/S$) in pure D0$_{22}$-Al$_3$Ti and W – M co-doping systems with an Al vacancy at the V$_1$ site.
The calculated DOS are given in Fig. 3a for the pure D0_{22}-AlTi, and in Fig. 3b-f for W-C, W-Si, W-Ge, W-Sn and W-Pb co-doping AlTi with an Al vacancy at the V_{1} site, respectively. In addition, both V_{1} and V_{2} defects are spontaneously formed when the Al vacancy occurs at V_{2} site, the vacancy formation energies of Al at V_{1} site are higher than that of V_{2} site, as shown in Table 2. The calculated DOS curve shows that the ternary W-atom strongly favors the Al site over the Ti site in the D0_{22} structure. Therefore, the substitution energies of W and Al in the ternary system are much lower than the single doping systems. It indicates that introducing W in pure D0_{22}-AlTi structure will conduce to the substitution of Ti by W.

**Vacancy formation energy.** The crystal model with an Al vacancy were created by removing an individual Al-atom from W – M co-doping supercell. The stability of the defected structures were studied by vacancy formation energy calculation after the atomic defects are relaxed completely. The formation energy of a neutral aluminum vacancy (hereafter simply referred to as an aluminum vacancy) (E_{V}) is estimated by the following equation (5):

\[ E_{V}(M) = E_{\text{def}} - E_{W-M} + \sum_{i} n_{i} \mu_{i} \]  

where E_{V}(M) is the vacancy formation energy, E_{def} is the total energy of D0_{22}-AlTi/W supercell containing one M-atom and one Al vacancy simultaneously and E_{W-M} is the total energy of W – M co-doping supercell. The last term represents the difference in the number of atoms from the W – M co-doping system, where n_{i} denotes the number of atoms to be taken from or inserted into the supercell in order to take account of point defect generation. If a corresponding atom is inserted into the supercell, n_{i} is positive and if such an atom is taken away from the supercell, n_{i} is negative. \mu_{i} is the chemical potential of these atoms in their stable bulk phases. The calculated defect formation energies are tabulated in Table 2.

From Table 2, it can be easily observed that the vacancy formation energies of Al at V_{1} site are higher than that at V_{2} site. For a W – M co-doping system, when the Al vacancy occurs at V_{2} site, the vacancy formation energies are negative under both Al-rich environment and Ti-rich environment, which indicates V_{2} defects can be formed spontaneously during the fabrication of the alloy. In addition, both V_{1} and V_{2} defects are spontaneously formed by a W-Pb co-doping under either Al-rich or Ti-rich environment. The results attribute to the fact that the W – M co-doping cluster plays a vital role in the formation of Al vacancies.

**Electronic states of defected structure.** The calculated DOS are given in Fig. 3a for the pure D0_{22}-AlTi, and in Fig. 3b-f for W-C, W-Si, W-Ge, W-Sn and W-Pb co-doping AlTi with an Al vacancy at the V_{1} site, respectively. \Delta n is introduced to indicate the valley of pseudogap. The value of \Delta n is the energy of the lowest position on the calculated DOS curve. Thus, the positive value means the psuedogap is higher than the Fermi level, while the negative value means the pseudogap is lower than the Fermi level.

### Table 1. The energies of M doping Al_{23}Ti (E_{M}) and W – M co-doping Al_{23}Ti (E_{W-M}).

| M   | C     | Si   | Ge   | Sn   | Pb   |
|-----|-------|------|------|------|------|
| E_{0} (eV) | −168.52 | −160.49 | −159.85 | −157.87 | −156.90 |
| ΔE | 1.945 | 0.795 | 0.595 | 0.515 | 0.315 |

**Vacancy formation energy.** The crystal model with an Al vacancy were created by removing an individual Al-atom from W – M co-doping supercell. In order to reduce the computation loads, we focus on the first-nearest neighbors, thus, the two possible Al vacancies are at V_{1} and V_{2} sites considering the system symmetry, shown as yellow spheres in Fig. 2a. The stability of the defected structures were studied by vacancy formation energy calculation after the atomic defects are relaxed completely. The formation energy of a neutral aluminum vacancy (hereafter simply referred to as an aluminum vacancy) (E_{V}) is estimated by the following equation (5):

\[ E_{V}(M) = E_{\text{def}} - E_{W-M} + \sum_{i} n_{i} \mu_{i} \]  

where E_{V}(M) is the vacancy formation energy, E_{def} is the total energy of D0_{22}-AlTi/W supercell containing one M-atom and one Al vacancy simultaneously and E_{W-M} is the total energy of W – M co-doping supercell. The last term represents the difference in the number of atoms from the W – M co-doping system, where n_{i} denotes the number of atoms to be taken from or inserted into the supercell in order to take account of point defect generation. If a corresponding atom is inserted into the supercell, n_{i} is positive and if such an atom is taken away from the supercell, n_{i} is negative. \mu_{i} is the chemical potential of these atoms in their stable bulk phases. The calculated defect formation energies are tabulated in Table 2.

From Table 2, it can be easily observed that the vacancy formation energies of Al at V_{1} site are higher than that at V_{2} site. For a W – M co-doping system, when the Al vacancy occurs at V_{2} site, the vacancy formation energies are negative under both Al-rich environment and Ti-rich environment, which indicates V_{2} defects can be formed spontaneously during the fabrication of the alloy. In addition, both V_{1} and V_{2} defects are spontaneously formed by a W-Pb co-doping under either Al-rich or Ti-rich environment. The results attribute to the fact that the W – M co-doping cluster plays a vital role in the formation of Al vacancies.

**Electronic states of defected structure.** The calculated DOS are given in Fig. 3a for the pure D0_{22}-AlTi, and in Fig. 3b-f for W-C, W-Si, W-Ge, W-Sn and W-Pb co-doping AlTi with an Al vacancy at the V_{1} site, respectively. \Delta n is introduced to indicate the valley of pseudogap. The value of \Delta n is the energy of the lowest position on the calculated DOS curve. Thus, the positive value means the psuedogap is higher than the Fermi level, while the negative value means the pseudogap is lower than the Fermi level.
level. The result is shown in Table 3. A clear pseudogap is observed in the D0_{22}-Al_{3}Ti (circled part in Fig. 3a), which indicates the strong bonding-antibonding separation. The result shows a strong hybridization existing in the D0_{22} structure as well as a strong directionality in bonding. Therefore, it is difficult to form the slip system in the tetragonal D0_{22} structure and leads to brittleness. The partial DOS of D0_{22}-Al_{3}Ti around the pseudogap was investigated, shown in Fig. 3g. From the edges of the gap, the splitting 3d orbitals could be observed clearly, thus, b_{1g} (d_{x}^{2}−d_{y}^{2}) energy is higher than a_{1g} (d_{z}^{2}) on the right edge, while b_{2g} (d_{xy}) energy is higher than e_{g} (d_{xy}, d_{yz}) on the left edge, which appears a typical tetragonal crystal field.

From Fig. 3b–f, by adding different M elements and forming a W−M co-doping cluster with an Al vacancy at V_{1} simultaneously, the pseudogap migrates from far above towards the Fermi level, indicated by the red arrows.

Table 2. The vacancy formation energies of W−M co-doping Al_{3}Ti when an Al vacancy forms at V_{1} site (E_{V1}) or V_{2} site (E_{V2}) under both Al-rich and Ti-rich environment.

|       | pure Al_{3}Ti | C      | Si     | Ge     | Sn     | Pb     |
|-------|---------------|--------|--------|--------|--------|--------|
| Δn(eV)| 0.876         | 0.798  | 0.684  | 0.678  | 0.587  | 0.125  |

Table 3. The position of the valley of pseudogap.

Figure 3. The calculated (DOS) of (a) pure D0_{22}-Al_{3}Ti, (b–f) W−M co-doping Al_{3}Ti with an Al vacancy at V_{1} site, W = C, Si, Ge, Sn and Pb, respectively. The calculated partial DOS of (g) pure D0_{22}-Al_{3}Ti, (h) W−Pb co-doping Al_{3}Ti (Note only 3d orbitals are presented here). All arrows indicate the pseudogap position.
The results show that there are less bonding states which may favor a D0_{22} to L1_2-like transition. To carry out a more in-depth and detailed study, partial DOS crossing the pseudogap of the W-Pb co-doping system was calculated and shown in Fig. 3h. Contributions from W and Pb to bonding electrons were investigated separately. On the right edge of the pseudogap, it is observed that W-atom contributes a lot to form strong hybridization between the d_{xy} and d_{x^2−y^2} levels. Similarly on the left edge of the pseudogap, the Pb-atom has a strong influence on rising the d_{xz} energy and d_{yz} energy towards the d_{xy} level (or a strong hybridization among these 3d orbitals). Therefore, the vacancy-induced 3d-orbital-splitting tend to facilitate a ductile L1_2-like structure, thus, c_{eg} (d_{x^2−y^2}, d_{xz}) and t_{2g} (d_{xy}, d_{xz}, d_{yz}).

To obtain the brittle to ductile transition, the tetragonal D0_{22} structure is expected to transform into an octahedral-like structure, which could be realized by either a shrinking along z-axis or an expanding on the xy-plane or both. By representing the ratio r of z-axis d to the xy-plane S, the change in structures are quantified, as shown in Fig. 2b. Taking pure D0_{22}-Al,Ti as the standard, it can be concluded that r decreased with the formation of Al vacancy at V_1 site, which indicates that the tetragonal crystal field tends to transform into an octahedral-like crystal field. As a result, the stable phase change from D0_{22} to L1_2-like ductile structures. When an Al vacancy forms at the V_2 site, S remains nearly a constant except for the W-C co-doping. The larger S in the W-C co-doping system is due to the small size of C. Among all M elements in Table 4, C is the only dopant whose size is smaller than that of Al (0.39 Å for Al^{10+}). More details will be outlined in Session 3 below.

### Discussion

In order to enable a brittle to ductile transition, we proposed and validated a W − M co-doping mechanism to (1) generate sufficient Al vacancies in D0_{22}-Al,Ti, and (2) simultaneously to manipulate specific electron energy levels to approach the high symmetry octahedral-like electronic structures. In particular, an equation for the lattice energy of W − M co-dopants is derived based on the E_{W−M} (eV) given in Table 1:

$$E_{W−M} = -170.3 + 9.44R_M^2$$

(6)

where $R_M$ is the ionic radius of M.

The calculated E_{W−M} based on equation (6) is $-170.1$, $-167.8$, $-167.6$, $-165.8$, $-164.6$ eV for M = C, Si, Ge, Sn and Pb respectively, which is very close to the DFT calculations, thus, $-169.9$, $-168.7$, $-167.9$, $-165.8$, $-164.6$ eV. Therefore, E_{W−M} is in proportional to the cross-section of an M-ion ($R_M^2$), or E_{W−M} is 2-dimensional size (or xy-plane) dependent only. This is a good indicator that a W − M co-doping may only manipulate the xy-plane while leaving out the z-direction untouched.

Similarly, an equation for the formation energy of V_2-W − M co-dopants is derived based on the E_{V_2} (eV) data given in Table 2:

For Al-rich: $E_{V_2} = -3.9(R_M - 0.39)^2$

(7)

For Ti-rich: $E_{V_1} = -0.55 - 3.9(R_M - 0.39)^2$

(8)

Both equations (7) and (8) reasonably reproduce DFT calculations shown in Table 2. We derived V_2-W − M equations only since they are stable (or having negative formation energy) for all the M elements. Like equation (6), both equations (7) and (8) are in proportion to the cross-section changes of a substitutional M-ion and an Al vacancy ($R_M − 0.39$). Once again, a V_2-W − M co-doping may only manipulate the xy-plane while leaving out the z-direction untouched. This 2-D manipulation function of W − M co-doping is the basis that enables a brittle (D0_{22}) to ductile (L1_2-like) transition, which can be applied not only for Al,Ti but all intermetals in general.

Finally, we have systematically investigated a series of W − M co-doping D0_{22}-Al,Ti (M = C, Si, Ge, Sn and Pb) intermetalics using first-principles calculation method. The site preference of W in pure D0_{22}-Al,Ti was first studied, it shows W (a d element) has a clear preference to substitute Al (a sp element) site due to the strong crystal field. Then, we confirmed the ([Al_3W]Ti) system is conductive to the subsequent doping of M-atom. Meanwhile, a M substitution of Ti reduces the stability of ([Al_3W]Ti) system, which might benefit the intercalation and deintercalation of Al during charge-discharge cycling in rechargeable Al battery. The two possible Al vacancies were also investigated. In comparison to the vacancy formation energies of Li-ion in Li_3N (−0.14 ~ 0.52 eV), the Al vacancies in W − M co-doped Al,Ti have much lower formation energies, therefore, high Al diffusivity is expected.

The DOS of W − M co-doping Al,Ti with an Al vacancy at the V_1 site were investigated. The results show the pseudogap migrates towards the Fermi level from far above, indicating a tendency to transform into ductile L1_2-like structure. By analyzing the partial DOS around the pseudogap, we found that W and Pb have almost independent contributions to the transition, thus, W mainly influences d_{x^2−y^2} and d_{yz} while Pb have a strong effect on d_{xy}, d_{xz} and d_{yz}. It shows the crystal splitting effect on the 3d orbitals plays a decisive role not only on the

### Table 4. Ionic Shannon radius ($R_M$) and the electronegativity (EN)²⁵

| M   | C  | Si | Ge | Sn | Pb | Al | Ti | W  |
|-----|----|----|----|----|----|----|----|----|
| R_M(Å) | 0.16 | 0.4 | 0.53 | 0.69 | 0.78 | 0.39 | 0.42 | 0.66 |
| EN   | 2.50 | 1.74 | 2.02 | 1.72 | 1.55 | 1.47 | 1.32 | 1.40 |

For Tirth: 05 53 9(0 39) (8)VM

For Arich: 39 (0 39) (7)VM W M co-doped Al,Ti have much lower formation energies, therefore, high Al diffusivity is expected.
formation but also the transformation of pseudogap. Therefore, this study contributes to the formation of a new field in physics to design mechanical properties from electronic structures via vacancy optimization.

**Methods**

Calculations were carried out within the framework of density functional theory (DFT)\textsuperscript{20}, using the projector-augmented wave (PAW) method\textsuperscript{21} and the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{22} for the exchange-correlation energy functional, via the Vienna ab initio Simulation Package (VASP)\textsuperscript{23}. We first calculated the equilibrium lattice parameters of the Al\textsubscript{3}Ti using plane-wave cutoff energy of 340 eV and a \(7 \times 7 \times 7\) k-point mesh in the Monkhorst-Pack scheme\textsuperscript{13} by using the \(2 \times 2 \times 1\) supercell including 32 atoms. In all calculations, self-consistency was achieved with a tolerance in the total energy of 0.01 meV, and the atom were relaxed until the forces were less than 0.01 eV/Å. The crystal structures were fully optimized by independently modifying lattice parameters and internal atomic coordinates.

**Data availability statement.** All data generated or analyzed during this study are included in this published article.

**References**

1. Jang, D. C. & Greer, J. R. Transition from a strong-yet-brittle to a stronger-and-ductile state by size reduction of metallic glasses. *Nature Mater* 5(3), 215–219 (2016).
2. Peterlik, H. et al. From brittle to ductile fracture of bone. *Nature Mater* 5(1), 52–55 (2006).
3. Ramos, L. et al. Structural signature of a brittle-to-ductile transition in self-assembled networks. *Phys. Rev. Lett.* 107(14) (2011).
4. Tallinen, T. & Mahadevan, L. Forced tearing of ductile and brittle thin sheets. *Phys. Rev. Lett.* 107(24) (2011).
5. Yuan, C. C. et al. NMR Signature of evolution of ductile-to-brittle transition in bulk metallic glasses. *Phys. Rev. Lett.* 107(23) (2011).
6. Wu, P. F. & Wu, T. Temperature-dependent modulus of resilience in metallic solids – calculated from strain-electron-phonon interactions. *J. Alloys Compd.* 705, 269–272 (2017).
7. Pan, Y. et al. Vacancy induced brittle-to-ductile transition of NbSi\textsubscript{3} alloy from first-principles. *Mater. Des.* 86, 259–265 (2015).
8. Yuan, Z. P., Cui, H. B. & Guo, X. F. First-principle calculation on mechanical and thermal properties of B2-NiSc with point defects. *J. Semicond.* 38(1), 5 (2017).
9. Niu, H. Y. et al. Extra-electron induced covalent strengthening and generalization of intrinsic ductile-to-brittle criterion. *Sci. Rep.* 2 (2012).
10. Pan, Y. et al. Influence of vacancy on structural and elastic properties of NbSi\textsubscript{2} from first-principles calculations. *Mater. Des.* 108, 13–18 (2016).
11. Shi, T. T. et al. Atomic diffusion mediated by vacancy defects in pure and transition element (TM)-doped (TM = Ti, Zr or Hf) L1(2) Al,Sc Mater. Des. 108, 529–537 (2016).
12. Hong, T. et al. Crystal-structure, phase-stability, and electronic-structure of Ti-Al intermetallics-TiAl\textsubscript{13}. *Phys. Rev. B.* 41(18), 12462–12467 (1990).
13. Milman, Y. V. et al. Mechanical behaviour of Al,Ti intermetallic and L1\textsubscript{2} phases on its basis. *Intermetallics* 9(9), 839–845 (2001).
14. Chen, Z. L. et al. Chemical bonding and pseudogap formation in D0(22) and L1(2) structure (V, Ti)Al\textsubscript{2}. *J. Phys. Chem. Solids.* 71(7), 946–951 (2010).
15. Frazier, W. E. & Benci, J. E. Crystal structure and phase relationships in as-cast and melt spun Al\textsubscript{3}Ti and Al\textsubscript{x}Ti plus copper. *Scripta Mater.* 25(10), 2267–2272 (1991).
16. Ghosh, G. et al. Stability and elastic properties of L1\textsubscript{2}-(Al,Cu)\textsubscript{3}(Ti,Zr) phases: Ab initio calculations and experiments. *Intermetallics* 15(1), 44–54 (2007).
17. Wei, X. P. et al. The electronic and magnetic properties of defects on half-metallic Ti\textsubscript{3}NiIn alloy. *J. Solid State Chem.* 233, 221–228 (2015).
18. Li, L. et al. First-principles study of Al/Al, Ti heterogenous nucleation interface. *Appl. Surf. Sci.* 307, 593–600 (2014).
19. Wu, S., Dong, Z. & Wu, P. Effect of transition metal (M = Co, Ni, Cu) substitution on electronic structure and vacancy formation of Li\textsubscript{11}Ni. *J. Mater. Chem.* 21(1), 165–170 (2010).
20. Loo, F. J. J. & Rieck, G. D. Diffusion in the titanium-aluminum system inter-diffusion between solid Al and Ti or Ti-Al alloys. *Acta. Metall.* 21(1), 61–71 (1973).
21. Raviravan, S., Desch, P. B. & Schwarz, R. B. Metastable phases in the Al\textsubscript{3}X (X = Ti, Zr, and Hf) intermetallic system. *Scripta Mater.* 25(11), 2513–2516 (1991).
22. Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140(4A), A1133–A1138 (1965).
23. Sridharan, S. & Nowotny, H. Studies in the ternary system Ti-Ta-Al and in the quaternary system Ti-Ta-Al-C. *Z. Metallkd.* 74, 468–472 (1983).
24. Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* 32(5), 751–767 (1976).
25. Alfred, A. L. & Rochow, E. G. Electronegativities of carbon, silicon, germanium, tin and lead. *J. Inorg. Nucl. Chem.* 5(4), 269–288 (1958).

**Acknowledgements**

The authors acknowledge the computational resources from the National Supercomputing Center in Tianjin (TH-1A System). P. Wu’s work on mechanical modeling is partially supported by the National Research Foundation, Prime Minister’s Office, Singapore, under its Marine Science Research & Development Programme (Award Number MSRDP-P28).

**Author Contributions**

M.K.Z., P.W., X.B. and Q.L.L. designed and coordinated the overall study. M.K.Z. and P.W. wrote the manuscript. Z.M.K. performed theoretical calculations with the help from P.W., X.B. and Q.L.L. All contributed to the discussions of the results.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.
