Effect of transition metal additives on electronic structure and elastic properties of TiAl and Ti$_3$Al

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We have studied the correlation between the electronic structure and elastic properties of γ-TiAl (space group $P4/mmm$, prototype AuCu) as well as α_2-Ti$_3$Al (space group $P6_3/mmc$, prototype Ni$_3$Sn) alloyed with VB (V, Nb, Ta), VIB (Cr, Mo, W), and VIIB (Mn) transition metals, using *ab initio* calculations. Upon alloying, the bulk modulus is increased as compared to unalloyed phases. This can be understood based on the partial density of states analysis. The bonding in γ-TiAl and α_2-Ti$_3$Al is mainly metallic, due to Ti *d*-Ti *d* interactions, and there is a weak covalent contribution, due to hybridization between Al *p* and Ti *d* orbitals. This increase in the bulk modulus is due to band filling. On the other hand, the values of the elastic constant C_{44} are comparable with or lower than those of γ-TiAl and α_2-Ti$_3$Al. Upon alloying, the metallic bonding character is enhanced and the covalent bonding character is reduced. The bulk-modulus-to-C_{44} ratio is hence larger as compared to the unalloyed substances. The largest value is obtained for the Mn substitution, resulting in a 13.5% and 19.6% increase for γ-TiAl and α_2-Ti$_3$Al, respectively. These results are of relevance to the tailoring of the mechanical properties of TiAl alloys.

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I. INTRODUCTION

TiAl alloys, composed of γ-TiAl (space group $P4/mmm$, prototype AuCu) and smaller amounts of α_2-Ti$_3$Al (space group $P6_3/mmc$, prototype Ni$_3$Sn), are used for high-temperature applications owing to their chemical stability, low density, and good oxidation resistance.[1] It terms of mechanical properties, γ-TiAl and α_2-Ti$_3$Al possess the bulk modulus of 112 and 113 GPa, respectively.[2] Broader application of TiAl alloys is limited due to their intrinsic brittleness.[1] This limitation has been addressed experimentally by alloying with transition metals as well as IIIA and IVA elements.[1,3] Hao and co-workers[3] have measured the site occupancy of V, Cr, Mn, Fe, Ni, Zr, Nb, Mo, Ta, Ga, and Sn in γ-TiAl and α_2-Ti$_3$Al using the atom location channeling enhanced microanalysis. For γ-TiAl, their results indicate that Zr, Nb, and Ta atoms occupy Ti sites, while Fe, Ni, Ga, and Sn atoms occupy Al sites. On the other hand, the site preference for V, Cr, and Mn was reported to be a function of the composition. For α_2-Ti$_3$Al, Ga and Sn atoms occupy Al sites, while V, Cr, Mn, Zr, Nb, Mo, and Ta atoms occupy Ti sites. These results were corroborated by analyzing the site preference of alloying elements in TiAl alloys based on *ab initio* calculations.[4–6] However, there are no theoretical studies addressing the elastic property changes in TiAl alloys induced by alloying.

In this work, *ab initio* calculations are used to determine the alloying element induced changes in electronic structure and elastic properties of γ-TiAl as well as α_2-Ti$_3$Al. The valence electron concentration of the alloying elements was systematically varied through substitution of Ti and Al with VB (V, Nb, Ta), VIB (Cr, Mo, W), and VIIB (Mn) transition metals. The bulk-modulus-to-C_{44} ratio is increased for all alloying elements as compared to the unalloyed TiAl phases. The largest value is obtained for the Mn substitution, resulting in a 13.5% and 19.6% increase for γ-TiAl and α_2-Ti$_3$Al, respectively. This can be understood based on

alloying element induced changes in the electron structure. It is our ambition to spark systematic experimental studies of the elastic and plastic properties with this contribution.

II. COMPUTATIONAL DETAILS

All calculations were carried out using density functional theory,[7] as implemented in the Vienna *ab initio* simulation package (VASP), wherein projector augmented wave potentials are employed.[8] The generalized-gradient approximation was applied in all calculations with the so-called Blöchl corrections for the total energy.[9] The integration in the Brillouin zone is done on special *k* points, determined according to the Monkhorst-Pack method.[10] Supercells containing 16 atoms (2×2×2 for γ-TiAl and 1×1×2 for α_2-Ti$_3$Al) were studied on a mesh of 7×7×7 irreducible *k* points. One host atom in the supercells was replaced with VB (V, Nb, Ta), VIB (Cr, Mo, W), and VIIB (Mn) transition metals, as shown in Fig. 1. The convergence criterion for the total energy was 0.01 meV within a 350 eV cutoff. All phases were relaxed with respect to atomic positions (internal free parameters), lattice parameter *a*, and *c*/*a* ratio. After relaxation, the equilibrium values for *a* and *c*/*a* were obtained by fitting the total energy versus *a* or *c*/*a* with third-order polynomials. The bulk modulus was obtained by fitting the energy-volume curves to the Birch-Murnaghan equation of states.[11] The elastic constant C_{44} was determined according to the method developed by Mehl *et al.*[12] for γ-TiAl and Fast *et al.*[13] for α_2-Ti$_3$Al. C_{44} is proportional to the shear modulus and can be used as a measure for the shear resistance.[14,15] Furthermore, the total and partial density of states (DOS) as well as the energy of formation[16–18] with respect to elements were calculated. The convergence of the energy of formation was evaluated for γ-TiAl for cutoff energies of 350, 400, 500, and 600 eV. The difference in energy of formation between the 350 eV cutoff and other investigated cutoff energies was between 0.1 and 1.4 meV/atom.
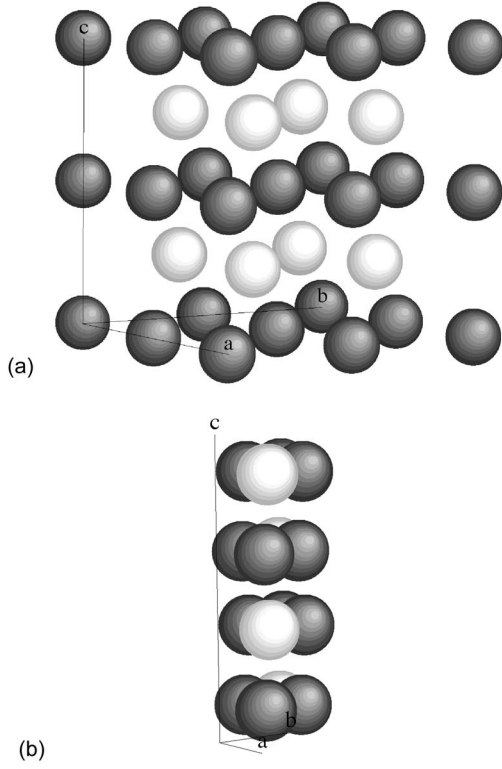
FIG. 1. Supercells used in this work: (a) $2\times2\times2$ for γ-TiAl (Ti and Al occupy $1a$ and $1d$ Wyckoff positions, respectively) and (b) $1\times1\times2$ for α_2-Ti$_3$Al (Ti and Al occupy $6h$ and $2c$ Wyckoff positions, respectively). a, b, and c designate primitive vectors. Bright and dark gray spheres represent Al and Ti atoms, respectively.

III. RESULTS AND DISCUSSIONS

Table I contains the calculated lattice parameters, bulk modulus, C_{44} elastic constant, and energy of formation for γ-TiAl alloyed with V, Nb, Ta, Cr, Mo, W, and Mn. The equivalent data for α_2-Ti$_3$Al is given in Table II. The energy of formation was determined for all alloying elements probing both sites (Ti and Al). The calculated lattice parameters for γ-TiAl and α_2-Ti$_3$Al deviate by 0.9% and 0.3%, respectively, from the previously reported experimental data.[19,20] Two important observations can be made by analyzing the energy of formation: site preference as well as stability of the ternary compound compared to the corresponding binary. For γ-TiAl, the substitution occurs at the Ti site for all elements studied with the exception of Cr and Mn. For the Cr substitution, the energy of formation difference between the Ti and Al site is not significant, so that Cr may occupy both sites, while Mn occupies the Al site. The stability of the ternary compound compared to γ-TiAl considering the preferred sites is decreased by $4-62$ meV/atom. For α_2-Ti$_3$Al, the Ti site is always preferred. The stability of the ternary compound compared to α_2-Ti$_3$Al considering the preferred sites is decreased by $2-52$ meV/atom. These data for the site preference of the alloying elements in γ-TiAl and α_2-Ti$_3$Al are consistent with the experimental results.[3] Furthermore, our results are also consistent with the calculated stability and site preference data for the alloying of γ-TiAl (Refs. [4] and [6]) and α_2-Ti$_3$Al.[6]

TABLE I. Lattice parameters (a and c/a), bulk modulus (B), C_{44} elastic constant, and energy of formation (E_{form}), with respect to elements for γ-TiAl alloyed with V, Nb, Ta, Cr, Mo, W, and Mn. Both sites (Ti and Al) were probed for all alloying elements.

	Site	a (Å)	c/a	B (GPa)	C_{44} (GPa)	E_{form} (eV/atom)
TiAl		4.003	1.014	112	126	−0.401
TiAl (V)	Ti	3.992	1.006	116	128	−0.371
TiAl (V)	Al	4.011	1.003	115	—	−0.342
TiAl (Nb)	Ti	4.001	1.019	117	126	−0.391
TiAl (Nb)	Al	4.022	1.014	115	—	−0.341
TiAl (Ta)	Ti	4.001	1.019	118	127	−0.379
TiAl (Ta)	Al	4.018	1.017	116	—	−0.337
TiAl (Cr)	Ti	3.989	0.999	117	127	−0.339
TiAl (Cr)	Al	4.011	0.994	118	—	−0.336
TiAl (Mo)	Ti	3.992	1.010	120	128	−0.383
TiAl (Mo)	Al	4.019	1.005	119	—	−0.362
TiAl (W)	Ti	3.994	1.010	122	128	−0.361
TiAl (W)	Al	4.021	1.006	121	—	−0.349
TiAl (Mn)	Ti	3.987	0.995	117	—	−0.381
TiAl (Mn)	Al	4.005	0.991	119	118	−0.397

The calculated bulk modulus and C_{44} values for γ-TiAl are 112 and 126 GPa, respectively, which accounts for the bulk-modulus-to-C_{44} ratio of 0.89. The experimental values[2] were reported to be 112 and 109 GPa, respectively, and our data deviate by 0.0–13.5%. In the case of α_2-Ti$_3$Al, the calculated bulk modulus and C_{44} values are 114 and 72 GPa, which accounts for the bulk-modulus-to-C_{44} ratio of 1.58.

TABLE II. Lattice parameters (a and c/a), bulk modulus (B), C_{44} elastic constant, and energy of formation (E_{form}), with respect to elements for α_2-Ti$_3$Al alloyed with V, Nb, Ta, Cr, Mo, W, and Mn. Both sites (Ti and Al) were probed for all alloying elements.

|	Site	a (Å)	c/a	B (GPa)	C_{44} (GPa)	E_{form} (eV/atom)
Ti$_3$Al		5.772	0.803	114	72	−0.279
Ti$_3$Al (V)	Ti	5.750	0.799	118	71	−0.255
Ti$_3$Al (V)	Al	5.770	0.801	117	—	−0.175
Ti$_3$Al (Nb)	Ti	5.765	0.808	118	68	−0.269
Ti$_3$Al (Nb)	Al	5.785	0.805	116	—	0.059
Ti$_3$Al (Ta)	Ti	5.766	0.808	120	69	−0.265
Ti$_3$Al (Ta)	Al	5.788	0.811	118	—	−0.172
Ti$_3$Al (Cr)	Ti	5.746	0.795	119	67	−0.227
Ti$_3$Al (Cr)	Al	5.761	0.798	119	—	−0.156
Ti$_3$Al (Mo)	Ti	5.757	0.802	121	65	−0.269
Ti$_3$Al (Mo)	Al	5.772	0.807	121	—	−0.175
Ti$_3$Al (W)	Ti	5.758	0.802	124	66	−0.254
Ti$_3$Al (W)	Al	5.774	0.806	123	—	−0.171
Ti$_3$Al (Mn)	Ti	5.744	0.791	119	63	−0.277
Ti$_3$Al (Mn)	Al	5.753	0.797	119	—	−0.207
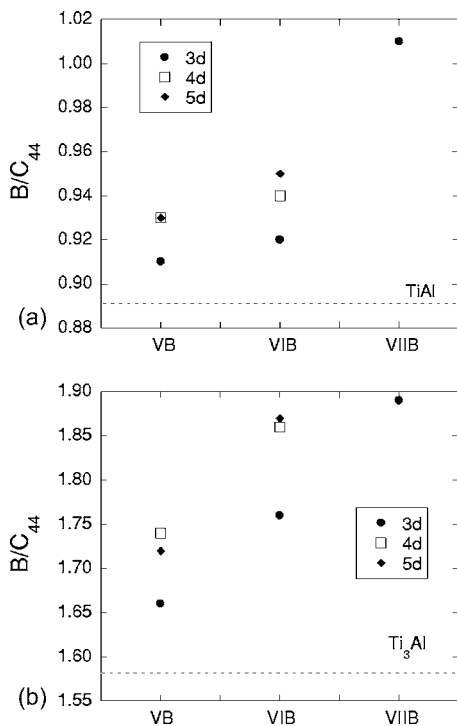
FIG. 2. Bulk modulus (B) vs C_{44} for (a) γ-TiAl and (b) α_2-Ti$_3$Al alloyed with VB transition metals (V, Nb, Ta), VIB transition metals (Cr, Mo, W), and VIIB transition metal (Mn). Dashed lines indicate the value for unalloyed phases.

The experimental values[2] were reported to be 113 and 64 GPa, respectively, and our data deviate by 0.9–12.5%. The magnitude of these deviations is typical for the elastic constants obtained by the density functional theory based methods.[13] It is known that the increase in the bulk-modulus-to-C_{44} ratio can be correlated to a decrease in brittleness.[14,15,21,22] Assuming that this notion is valid, the toughness of these TiAl phases can be improved by alloying with transition metals. As γ-TiAl and α_2-Ti$_3$Al are alloyed with VB, VIB, and VIIB transition metals, the bulk modulus increases from 116 to 122 GPa and from 118 to 124 GPa, respectively (see Table I and Table II). For these substitutions, the value of C_{44} is in the range of 118–128 and 63–71 GPa, respectively, which is comparable with or lower than those of the unalloyed phases (see Table I and Table II). This accounts for larger bulk-modulus-to-C_{44} ratios as compared to the unalloyed phases. In Fig. 2, the bulk-modulus-to-C_{44} ratio is given for γ-TiAl and α_2-Ti$_3$Al. As the valence electron population is increased, substituting Ti (or Al) with transition metals from groups VB to VIIB, the bulk-modulus-to-C_{44} ratio increases. The largest bulk-modulus-to-C_{44} ratio for γ-TiAl is obtained for the Mn substitution and the value is 1.01, accounting for an increase of 13.5%. The largest bulk-modulus-to-C_{44} ratio for α_2-Ti$_3$Al is also obtained for the Mn substitution, with a value of 1.89, which is an increase of 19.6%. As the valence electron population increases, it is to be expected that the bulk modulus increases, as is found here (see Table I and Table II), due to band filling effects.[23,24] In order to shed light on the valence electron induced changes of the bulk-modulus-to-C_{44} ratio, we study
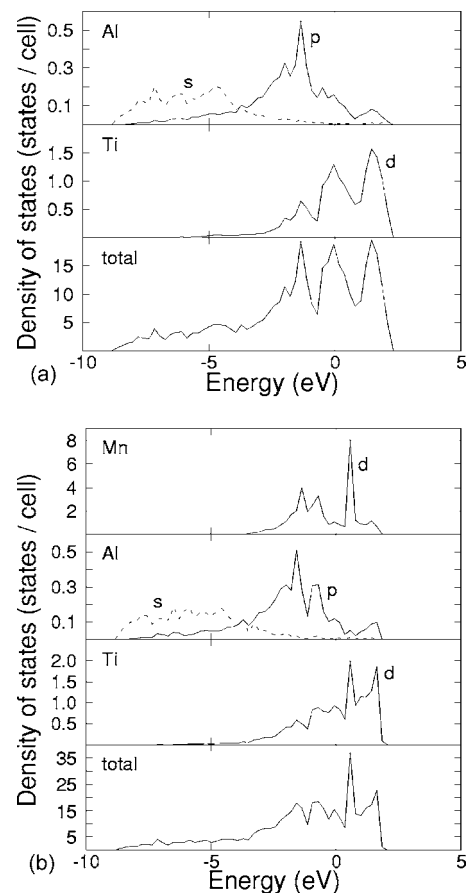

FIG. 3. Total and partial density of states for (a) γ-TiAl and (b) γ-TiAl alloyed with Mn, as obtained by the VASP code. Mn occupies the Al site. Fermi level is set to 0 eV.

the electronic structure of these alloyed TiAl phases.

In Fig. 3, the total and partial density of states data are given for γ-TiAl and γ-TiAl alloyed with Mn, since the Mn substitution provides the largest increase in the bulk-modulus-to-C_{44} ratio. It is obvious that the bonding character is metallic since the Fermi level is occupied and the Ti d-Ti d interaction dominates. There is also overlapping between Al p and Ti d orbitals from approximately −3 eV up to the Fermi level. This accounts for a covalent contribution to the overall bonding character. This contribution is rather small since overlapping occurs in a limited range and a significantly smaller amount of states is occupied, as compared to the metallic contribution. As Al is replaced with Mn, the Ti d-Al p interaction is reduced, while the Ti d-Mn d interaction increases. Furthermore, hybridization between Mn d and Al p states is observed. Hence, as Mn is introduced into γ-TiAl, the bonding in-plane is strengthened due to the directional Mn d-Al p interaction, while the bonding in the tetragonal c directions is weakened due to more pronounced nondirectional Ti d-Mn d interaction. These results are consistent with previous theoretical analysis.[4] The previously reported experimental observation that the ductility of TiAl alloys can be increased by alloying with V, Cr, and Mn (Ref. 3) can be understood based on the above analysis of the alloying element induced changes in nature and direction of the chemical bonding.
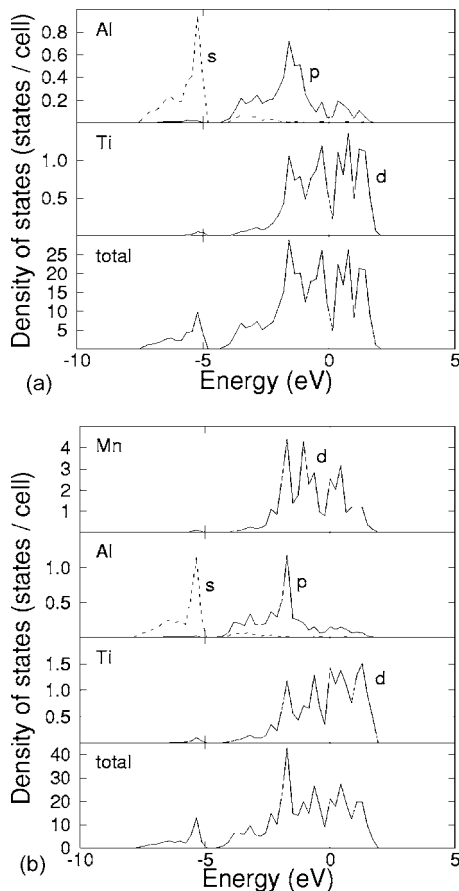
FIG. 4. Total and partial density of states for (a) α_2-Ti$_3$Al and (b) α_2-Ti$_3$Al alloyed with Mn. Mn occupies the Ti site. Fermi level is set to 0 eV.

In Fig. 4, the total and partial density of states data are given for α_2-Ti$_3$Al and α_2-Ti$_3$Al alloyed with Mn. Again, Mn is chosen for this comparison since it provides the largest increase in the bulk-modulus-to-C_{44} ratio. The dominating bonding character is metallic since the Fermi level is occupied and the Ti d-Ti d interaction plays the most important role. Also, there is overlapping between Al p and Ti d states from approximately -4 eV up to the Fermi level. This is consistent with a covalent, and hence, directional bonding contribution. However, this is smaller than the metallic, and

hence, nondirectional bonding contribution, since there are fewer electronic states involved. As Al is replaced with Mn, the directional Ti d-Al p interaction is reduced, while the nondirectional Ti d-Mn d interaction is enhanced. This is consistent with the behavior of γ-TiAl and the calculated bulk-modulus-to-C_{44} ratio, as discussed above. Hence, by alloying with Mn, both γ-TiAl and α_2-Ti$_3$Al increase their bulk-modulus-to-C_{44} ratio, which may improve the ductility of these phases. Thus, the physical mechanisms leading to the above discussed changes in bulk-modulus-to-C_{44} ratio are identical. Alloying of γ-TiAl and α_2-Ti$_3$Al with group VB, VIB, and VIIB transition metals results in characteristic changes in chemical bonding. The evolution of the elastic properties in compression and shearing can be understood by analyzing the nature and the direction of the chemical bonding of the alloy in comparison to the unalloyed compound.

IV. CONCLUSIONS

Using *ab initio* calculations, we have studied the correlation between electronic structure and elastic properties of γ-TiAl and α_2-Ti$_3$Al alloyed with VB, VIB, and VIIB transition metals. Upon alloying, the bulk modulus is increased as compared to unalloyed phases. This can be understood based on the alloying induced changes in electronic structure. The bonding in γ-TiAl and α_2-Ti$_3$Al is mainly metallic, due to nondirectional Ti d-Ti d interactions, with weak covalent contributions, due to the directional Al p and Ti d interactions. The increase in the bulk modulus is due to band filling. On the other hand, the values of C_{44} are comparable with or lower than those of γ-TiAl and α_2-Ti$_3$Al. Upon alloying, the nondirectional metallic bonding character is enhanced and the directional covalent bonding character is reduced. The bulk-modulus-to-C_{44} ratio is hence larger in comparison to the unalloyed substances, the largest value being obtained for the Mn substitution. These results are important for the tailoring of the mechanical properties of these TiAl alloys.

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