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Stability of $L2_1$ $(NiM)_2TiAl$ (M=Co, Fe) in high-entropy alloys

Shanshan Liu [a], Peiyu Cao [b], De-Ye Lin [c, d, *], Fuyang Tian [a, **]

[a] Institute for Applied Physics, University of Science and Technology Beijing, Beijing 100083, China
[b] State Key Laboratory for Advanced Metals and Materails, University of Science and Technology Beijing, Beijing 100083, China
[c] Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
[d] Software Center for High Performance Numerical Simulation, China Academy of Engineering Physics, Beijing 100088, China

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ABSTRACT

The $L2_1$ $(NiCo)_2TiAl$ phase plays a key role in the excellent mechanics of 3d high-entropy alloys. In this work, we investigate the phase stability and intrinsic mechanical properties of $L2_1$ $(Ni_xM_{1-x})_2TiAl$ (M = Co, Fe, $x = 0-1$) alloys by using *ab initio* methods. The phonon dispersion relations suggest that the thermodynamic stability of $L2_1$ Ni_2TiAl, Co_2TiAl and Fe_2TiAl as well as Y-type NiTiCoAl, NiTiFeAl and CoTiFeAl intermetallic compounds. The formation enthalpy and the energy contribution from vibrational entropy indicated that $(NiCo)_2TiAl$ is easier to form with respect to $(NiFe)_2TiAl$ and $(CoFe)_2TiAl$. With the increase of the Co content, both the ductility and Young's modulus of $L2_1$ $(Ni_{1-x}Co_x)_2TiAl$ ($x = 0-1$) alloy decrease, while anisotropy become strong. The Co content has no almost effect on the ductility, Young's modulus and anisotropy of the Y-type $(Ni_{1-y}Co_y)Ti(Ni_yCo_{1-y})Al$ ($y = 0-0.5$) solid-solution alloys, whereas the $(Ni_{1-y}Fe_y)Ti(Ni_yFe_{1-y})Al$ ($y = 0-0.5$) solid solutions show different ductility and anisotropy, compared with NiTiFeAl intermetallic compound.

1. Introduction

Since single-phase high entropy alloy was reported in 2004 [1,2], the extensive 3d high-entropy alloys (HEAs) composed of 3d transition metals have been studied extensively, due to their special phase stability and excellent mechanical behaviors [3–14]. Although HEAs were considered to be single-phase alloys, intermetallic compound precipitates with B2, $L1_2$, or $L2_1$ structures, were observed in 3d HEAs through XRD measurements [15–18]. Some second phases are beneficial to the mechanical behavior of HEAs. For instance, the $L2_1$ Huesler phase enhances resistance in multi-phase alloys. The limited slip in $L2_1$ phase strengthens the alloy but makes alloys brittle in the low room temperature. The $L2_1$ ordered intermetallic phase was observed in 3d HEAs with various Ti and Al contents, for examples, CoCrCuFeNiTiAlSi and $(FeNiCoCr)_{1-x-y}Ti_xAl_y$ HEAs [18,19], etc.

Due to the complicated interaction between several (above five) alloying elements, it is rather difficult to determine which alloying element and how much its chemical composition stabilize the $L2_1$ phase. Similarly it is not easy to determine the lattice site preference of alloying atoms. Choudhuri reported $L2_1$ phase composed of 38.8% Ni, 23.4% Al, 11.5% Ti, 11.1% Co, 7.9% Fe et al. [18]. Lu et al. recently observed the $(NiCo)_2TiAl$ Heusler particles formed along grain boundaries in $(FeNiCoCr)_{1-x-y}Ti_xAl_y$ HEAs [19].

With the above consideration, we use the density functional theory based *ab initio* methods to investigate the stability and intrinsic mechanical behaviors of $L2_1$ $(Ni_{1-x}M_x)_2TiAl$ and Y-type $(Ni_{1-y}M_y)Ti(Ni_yM_{1-y})Al$ (M = Co, Fe, $x = 0-1$, $y = 0-0.5$) alloys. We calculate the phonon dispersion, the vibrational entropy and the formation enthalpy to determine the lattice site preference of alloying elements to form the $L2_1$ $(NiM)_2TiAl$ phase (M = Co, Fe). As a function of the M content, we investigate the elastically mechanical behaviors of $L2_1$ $(Ni_{1-x}M_x)_2TiAl$ and Y-type $(Ni_{1-y}M_y)Ti(Ni_yM_{1-y})Al$ (M = Co, Fe, $x = 0-1$, $y = 0-0.5$) alloys.

The rest of the work is organized as follows. We present the details of the *ab initio* calculations in Sec. 2. The phase stability and elastic properties are presented in Sec. 3. We conclude our work in Sec. 4.

2. Calculated method

2.1. CASTEP

In the present study of the equilibrium structure of Ni-Co-Fe-Ti-

* Corresponding author. Institute for Applied Physics, University of Science and Technology Beijing, Beijing 100083, China.
** Corresponding author.
E-mail addresses: lin_deye@iapcm.ac.cn (D.-Y. Lin), fuyang@ustb.edu.cn (F. Tian).

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Al serial intermetallic compounds, we employed Cambridge Sequential Total Energy Package (CASTEP) [20] implemented in Materials Studio 2018 based on the density functional theory [21,22] within the spin polarized generalized gradient approximation, treated by Perdew-Burke-Ernzerhof exchange-correlation potentials [23]. The on-the-fly-generated (OTFG) ultrasoft pseudopotentials were used to represent the interactions between the ionic cores and the valence electrons. The plane wave cutoff energy is 500 eV. In the process of electronic minimization, the SCF tolerance is 1×10^{-6} eV/atom and the Pulay scheme was employed for density mixing. The Brillouin zone sampling was performed using special *k* points generated by Monkhorst-Pack scheme [24] with density parameters 0.02/Å. The BFGS algorithm was used to optimize the configurations including the atomic position and cell shape. A high convergence tolerance level (the energy is about 1.0×10^{-6} eV/atom, the maximum force is about 0.03 eV/Å, and the maximum stress is about 0.05 GPa) is also chosen. Note that we do not list the magnetic moments of alloying element, due to their small values in Ni-Ti-Co-Al and Ni-Ti-Fe-Al alloys.

The elastic constants describe the material's response to an applied stress, *i.e.* conversely stress required to maintain a given deformation. In *ab initio* calculations, one can set either the stress or the strain to a finite value, re-optimizing any free parameters and calculate strain or stress, further extract the elastic constants. In the present calculations, we used the volume-conserving strain and calculated the resulting stress for the unit cell without optimization.

The phonon dispersion was calculated by using the finite displacement method [25]. The formed supercell contains 108 atoms for $L2_1$ and Y-type structure.

2.2. EMTO-CPA

For the $L2_1$ $(Ni_{1-x}M_x)_2TiAl$ and Y-type $(Ni_{1-y}M_y)Ti(Ni_yM_{1-y})Al$ (M = Co, Fe, $x = 0–1$, $y = 0–0.5$) solid-soliton alloys, the density functional theory based exact muffin-tin orbitals (EMTO) method [26] in combination with the coherent potential approximation (CPA) [27] was employed. The Kohn–Sham equations [22] were solved within the scalar-relativistic and soft-core scheme [26]. The PBE exchange–correlation density functional was used to obtain the charge density and the total energy. The EMTO basis set included *s*, *p*, *d*, and *f* states. The Green's function was calculated for 24 complex energy points distributed exponentially on a semicircular contour including the valence states. In the irreducible wedge of the bcc Brillouin zone, we used the uniform k-point mesh $21 \times 21 \times 21$ for the $L2_1$ lattice structure.

The equilibrium volume and bulk modulus from the forth-order Birch-Murnaghan equation of state (*i.e.* the energy as a function of volume). Then the elastic constants c_{11}, c_{12} and c_{44} were determined by calculating the total energy as a function of volume-conserving lattice strains. With the Voigte-Reusse-Hill averaging method, we calculated the polycrystalline elastic moduli (shear modulus *G*, Young's modulus *E*), Poisson's ratio *v* and Zener ratio A_Z [21].

3. Results and discussion

3.1. M_2TiAl (M = Ni, Co, Fe) and NiTiMAl (M = Co, Fe) intermetallic compounds

Table 1 lists the equilibrium lattice parameter, bulk modulus, the formation enthalpy and elastic constants for the M_2TiAl (M = Ni, Co, Fe) and NiTiMAl (M = Co, Fe). Note that the Ni-Ti-*M*-Al quaternary compound can form three different atomic arrangements (Ni-*M*-Ti-Al, Ni-Ti-*M*-Al, Ni-*M*-Al-Ti) of equimolar quaternary Heusler alloy in the Y-type structure [28]. The most possible configuration is the arrangement of Ni-Ti-*M*-Al, where the number valence electrons of M is smaller than that of Ni.

Table 1
The equilibrium lattice parameter **a** (in unit of Å), bulk modulus *B* (in unit of GPa), the formation enthalpy ΔH (in unit of eV) and three independent elastic constants c_{ij} (in unit of GPa) for the M_2TiAl (M = Ni, Co, Fe) and NiTiMAl (M = Co, Fe) intermetallic compounds.

Method	*a*	*B*	ΔH	c_{11}	c_{12}	c_{44}	c'	$(c_{12}-c_{44})$
Ni_2TiAl								
EMTO	5.911	166.9		244.5	128.2	109.8	58.1	18.3
CASTEP	5.905	164.5	−2.501	192.0	150.7	100.2	41.3	50.5
Ref.[a]	5.90	164.0		223	135	104	44.0	31.0
Co_2TiAl								
EMTO	5.844	190.8		277.0	147.7	130.6	64.6	17.0
CASTEP	5.837	180.5	−2.473	274.6	133.4	123.4	70.6	10.0
Ref.[b]	5.848	190.0		214.0	177.9	122.1	18	55.8
Fe_2TiAl								
EMTO	5.840	187.2		350.7	125.4	136.6	122.7	−8.8
CASTEP	5.833	183.4	−1.906	302.2	124.0	117.6	89.1	6.4
Ref.[c]	5.858	197.8		331.5	130.3	120.7	55.6	9.6
NiTiCoAl								
EMTO	5.877	174.9		250.5	137.1	118.2	56.7	18.9
CASTEP	5.866	173.4	−2.380	223.3	148.5	110.1	37.4	19.2
NiTiFeAl								
EMTO	5.865	174.1		232.2	145.1	114.3	43.6	30.8
CASTEP	5.865		−2.146	213.9	143.3	111.1	35.3	32.2
CoTiFeAl								
EMTO	5.813	188.2		394.4	82.7	124.7	155.9	−42.0
CASTEP	5.809	189.5	−2.415	357.9	105.2	128.5	126.4	−23.3

[a] Reference [30].
[b] Reference [29].
[c] Reference [31].

Both lattice parameter and bulk modulus from the CASTEP and EMTO methods are consistent excellently with each other (the error is under 1%). The present equilibrium lattice parameters are in good agreement with the available theoretical and experimental results [29–31]. The formation enthalpy is calculated as $\Delta H = (E(\text{M2TiAl}) - 2E(\text{M}) - E(\text{Ti}) - \text{E(Al)})/4$, and $\Delta H = (E(\text{NiTiMAl}) - E(\text{Ni}) - E(\text{Ti}) - E(\text{M}) - E(\text{Al}))/4$, where $E(M_2TiAl)$ is the total energy of $L2_1$ M_2TiAl intermetallic compounds, E(M) or E(M) the energy of M with its ground-state structure (fcc for Ni and Al, hcp for Co, bcc for Fe), E(Ti) the energy of hcp Ti, and E(Al) for the energy of fcc Al. Ni_2TiAl has the most negative formation enthalpy among M_2TiAl compounds. This suggests that Ni_2TiAl and Co_2TiAl may be formed easily in the 3d HEAs. As compared to NiTiFeAl, the NiTiCoAl and CoTiFeAl alloys have more negative formation enthalpy.

According to the elastic stability condition of the cubic crystals ($c_{44} > 0$, $c_{11} > |c_{12}|$, and $c_{12}+2c_{12} > 0$), the present calculated elastic constants all satisfy the stability criterion (see Table 1), indicating that these compounds are thermodynamically stable. Due to the different deformation for the calculation of elastic constants and the different pseudopotentials employed in the EMTO and CASTEP calculations, the calculated elastic constants (c_{11}, c_{12}, c_{44} and c') are slightly different. The (c_{12}-c_{44}) values from EMTO and CASTEP are consistent with each other.

Fig. 1 shows the phonon dispersion of the considered intermetallic compounds. We plotted the phonon dispersion branch along the high-symmetry points. Due to the four atoms in unit cell of $L2_1$ crystal structure, total 12 phonon dispersion branches are produced, with three acoustical models and 9 optical models. The degeneracy gives rise to reduced number of phonon dispersion relations along each vibration. There exists no imaginary phonon frequency in the phonon density of state and whole Brillouin zone. These phonon dispersion relation calculations suggest that all intermetallic compounds are thermodynamic stable. Although Ni_2TiAl and CoTiFeAl have more negative formation enthalpy, the