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Supplementary Materials: First Principles Calculation of the Influence of Alloying on the Phase Stability, Elasticity, and Thermodynamic Properties of the MoNbTiVX (X = Al/Cr) Refractory High-Entropy Alloy

Lin Chen [1,2,3,†], Weijun Li [2,3,†], Weihe Shi [2,3], Liuqing Liang [2,3], Jinghui Sun [2,3], Chengchu Yin [4], Jiafei Yi [2,3], Xuming Zhang [2,3], Peilin Qing [2,3], Alin Cao [2,3], Xiaowei Zhang [1,*] and Hongxi Liu [1,*]

1 Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China; linchen_chn@vip.126.com
2 Guangxi Key Laboratory of Green Manufacturing for Ecological Aluminum Industry, Baise University, Baise 533000, China; liweijun_bsu@163.com (W.L.); shiweihe@bsuc.cn (W.S.); 02xbllq@163.com (L.L.); sjh270349234@bsuc.edu.cn (J.S.); yijiafei@bsuc.edu.cn (J.Y.); zhangxuming3000@bsuc.edu.cn (X.Z.); plqing110@163.com (P.Q.); caoalin@163.com (A.C.)
3 Engineering Research Center of Advanced Aluminium Matrix Materials of Guangxi Province, Baise University, Baise 533000, China
4 Guangxi Zhongke Petrochemical Research Institute Testing Co., Ltd., Nanning 530105, China; 15977149047@163.com
* Correspondence: zhxw72@163.com (X.Z.); piiiliuhx@sina.com (H.L.)
† These authors contributed equally to this work.

Table S1. The physical meanings of each symbol are in Table 1.

Calculating expressions	Symbols	Ref.
$\Delta S_{\text{mix}} = -R\sum_{i=1}^{n} c_i \ln c_i$	Where R (=8.314 JK−1 mol−1) is the gas constant, c_i is the molar fraction of the ith component, and n is the total number of the constituent elements.	[30]
$\Delta H_{\text{mix}} = \sum_{i,j=1,i\neq j}^{n} 4H_{\text{mix}}^{\text{AB}} c_i c_j$	Where $H_{\text{mix}}^{\text{AB}}$ is the mixing enthalpy of binary liquid AB alloys; c_i and c_j are the molar fraction of A and B in the high entropy alloys, and n is the total number of the constituent elements.	[31]
$\delta = 100 \times \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$	Where c_i is the molar fraction of the ith component, $\bar{r}$ is the average atomic radius and r_i is the ith atomic radius, and n is the total number of the constituent elements.	[32]
$\Omega = \frac{T_{\text{m}}\Delta S_{\text{mix}}}{\lvert\Delta H_{\text{mix}}\rvert}$	Where T_{m} is the melting temperature of n-element alloys, which is calculated using mixing rules: $T_{\text{m}} = \sum_{i=1}^{n} c_i (T_m)_i$, here, $(T_m)_i$ is the melting point of the ith component of the alloy.	[32]
$VEC = \sum_{i=1}^{n} c_i \left(VEC\right)_i$	Where c_i is the molar fraction of the ith component, $\left(VEC\right)_i$ is the VEC of the ith component, and n is the total number of the constituent elements.	[33]
$\Delta\chi = \sqrt{\sum_{i=1}^{n} c_i \left(\chi_i - \bar{\chi}\right)^2}$ $\bar{\chi} = \sum_{i=1}^{n} c_i \chi_i$	Where c_i is the molar fraction of the ith component, χ_i is the Pauling electronegativity for the ith element, and $\bar{\chi}$ is the averaged electronegativity.	[34]

$$\begin{cases} C' = \left(C_{11} - C_{12}\right)/2 \\ B = B_V = B_R = \left(C_{11} + 2C_{12}\right)/3 \\ S_V = \left(C_{11} - C_{12} + 3C_{44}\right)/5 \\ S_R = \left[5\left(C_{11} - C_{12}\right)C_{44}\right]/\left[3\left(C_{11} - C_{12}\right) + 4C_{44}\right] \\ S = S_H = \left(S_V + S_R\right)/2 \\ Y = 9BS/\left(3B + S\right) \\ v = \left(3B - 2S\right)/\left(6B + 2S\right) \end{cases} \tag{S1}$$

$$A_{VR} = \frac{G_V - G_R}{G_V + G_R} \tag{S2}$$

$$A^{\mathrm{U}} = 5\frac{G_V}{G_G} + \frac{B_V}{B_R} - 6 \geqslant 0 \tag{S3}$$

The free energy $G(p, T)$ of the equilibrium structure is obtained by finding the minimum value of G^* at a given pressure p and temperature (T) [50]:

$$G\left(p,T\right) = \min_{\boldsymbol{x},V} G^*\left(\boldsymbol{x},V;p,T\right) \tag{S4}$$

By using equation (S4), the internal coordinates $x(p, T)$ and equilibrium volume $V(p, T)$ of the equilibrium structure, as well as the equilibrium Gibbs function $G(p, T)$, can be obtained. In the harmonic model, the vibration in the crystal is considered as a gas with $3nN$ non-interacting phonons, with a volume-independent frequency of ω_j, where n is the number of atoms in each primitive cell, and N is the number of cells in the macroscopic solid. In QHA, the non-equilibrium Helmholtz free energy is[50]:

$$\begin{cases} F^*\left(\boldsymbol{x},V;T\right) = E_{static}\left(\boldsymbol{x},V\right) + F^*_{vib}\left(\boldsymbol{x},V;T\right) \\ F^*_{vib}\left(\boldsymbol{x},V;T\right) = \sum_{j=1}^{3nN}\left[\frac{\omega_j}{2} - k_B T \ln\left(1 - e^{-\omega_j/k_B T}\right)\right] \end{cases} \tag{S5}$$

Among them, the vibration frequency ω_j depends on the crystal geometry (x, V). Once the equilibrium volume is known, many thermodynamic properties can be directly derived from F^* equation (S5) and $G = U + PV - TS$, such as equilibrium entropy (S_{equi}), Gibbs free energy (G), constant heat capacity (C_{v}), and isothermal bulk modulus (B_T) [51]:

$$\begin{cases} S_{equi} = S_{equi}\left(V\left(P,T\right),T\right) = -\left(\frac{\partial F}{\partial T}\right)_V = \sum_j\left[-k_B \ln\left(1 - e^{-\omega_j/k_B T}\right) + \frac{\omega_j}{T}\frac{1}{e^{\omega_j/k_B T} - 1}\right] \\ U = U\left(V\left(P,T\right),T\right) = F + TS_{equi} = E_{\mathrm{static}} + \sum_j \frac{\omega_j}{2} + \frac{\omega_j}{e^{-\omega_j/k_B T} - 1} \\ C_{\mathrm{v}} = C_{\mathrm{v}}\left(V\left(p,T\right),T\right) = \left(\frac{\partial U}{\partial T}\right)_V = \sum_j C_{\mathrm{v},j} = \sum_j k_B\left(\frac{\omega_j}{k_B T}\right)^2 \frac{e^{-\omega_j/k_B T}}{\left(e^{-\omega_j/k_B T} - 1\right)^2} \\ B_T = -V\left(\frac{\partial p}{\partial V}\right)_T = V - \left(\frac{\partial^2 F}{\partial V^2}\right)_T \end{cases} \tag{S6}$$

In the QHA model, volume derivatives can also be used to calculate the Grüneisen parameter γ [50]. When the Grüneisen parameter γ is known, the thermal expansion coefficient α, constant heat capacity (C_p), and adiabatic bulk modulus (B_S) are calculated as follows[50]:

$$\begin{cases} \gamma = -\dfrac{V}{C_v T}\left(\dfrac{\partial(-TS)}{\partial V}\right)_T \\ \alpha = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p = \dfrac{\gamma C_v}{V B_T} \\ C_p = \left(\dfrac{\partial H}{\partial T}\right)_p = C_v(1+\gamma\alpha T) \\ B_S = -V\left(\dfrac{\partial p}{\partial V}\right)_S = V\left(\dfrac{\partial^2 U}{\partial V^2}\right)_S = B_T(1+\gamma\alpha T) \end{cases} \quad \text{(S7)}$$

$$\begin{cases} 2d\sin\theta = \lambda \\ d = a/\sqrt{h^2+k^2+l^2} \\ a = \lambda\sqrt{h^2+k^2+l^2}/(2\sin\theta) \end{cases} \quad \text{(S8)}$$

Among them, d is the interplanar spacing, in Å; θ is the angle between the X-ray and the corresponding crystal plane, in degrees (°); λ it is the wavelength of the incident beam (here, VESTA software powder diffraction calculation is based on Cu target material), λ = 1.5406 Å, a is the lattice constant in Å, and (hkl) is the crystal plane index.

$$H_{\text{form}} = \frac{1}{\sum_{i=1}^{n} x_i}\left(E_{\text{total}} - \sum_{i=1}^{n} x_i E_{\text{solid}}^{M_i}\right) \quad \text{(S9)}$$

Among them, E_{total} represents the total energy of the optimized crystal cell structure, x_i represents the number of atoms contained in the alloy element M_i in the system, and $E_{\text{solid}}^{M_i}$ represents the energy of a single M atom in the solid state, all in eV/atom units[43].

$$E_{\text{coh}} = \frac{1}{\sum_{i=1}^{n} x_i}\left(E_{\text{total}} - \sum_{i=1}^{n} x_i E_{\text{atom}}^{M_i}\right) \quad \text{(S10)}$$

Among them, $E_{\text{atom}}^{M_i}$ it represents the energy of isolated atom M_i in the system, obtained from the alloy structure optimization result data file, and its unit is eV/atom[43].

For cubic crystals, the anisotropy of bulk modulus B, shear modulus S, and Young's modulus Y can be calculated according to equation (S11) [3].

$$\begin{cases} 1/B = (S_{11}+2S_{12})(l_1^2+l_2^2+l_3^2) \\ 1/S = S_{44} + (8S_{11}-S_{12}-S_{44})(l_1^2l_2^2+l_2^2l_3^2+l_1^2l_3^2) \\ 1/Y = S_{11} - (2S_{11}-2S_{12}-S_{44})(l_1^2l_2^2+l_2^2l_3^2+l_1^2l_3^2) \end{cases} \quad \text{(S11)}$$

Among them, S_{ij} is the elastic flexibility coefficient of the alloy (S_{ij} is the inverse matrix of C_{ij}), and l_1, l_2, and l_3 are the cosines in the three directions of the a, b, and c axes, respectively, which can be represented as $l_1 = \sin\theta\cos\varphi$, $l_2 = \sin\theta\sin\varphi$, and $l_3 = \cos\varphi$.

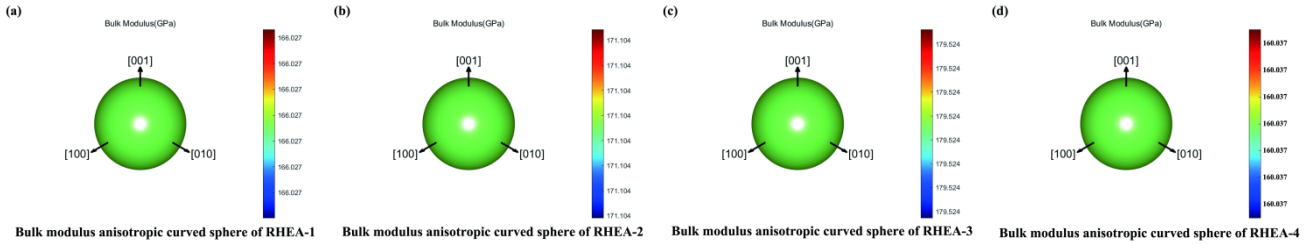

Figure S1. 3D spherical graph of bulk modulus (*B*) for RHEAs: (a) RHEA−1; (b) RHEA−2; (c) RHEA−3; (d) RHEA−4.

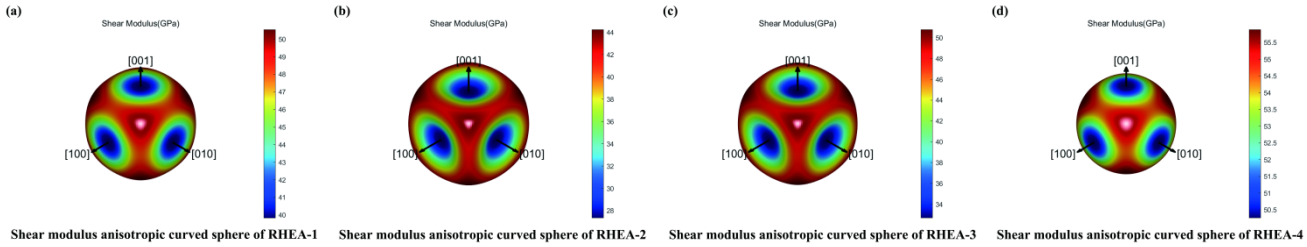

Figure S2. 3D spherical graph of shear modulus (*S*) for RHEAs: (a) RHEA−1; (b) RHEA−2; (c) RHEA−3; (d) RHEA−4.

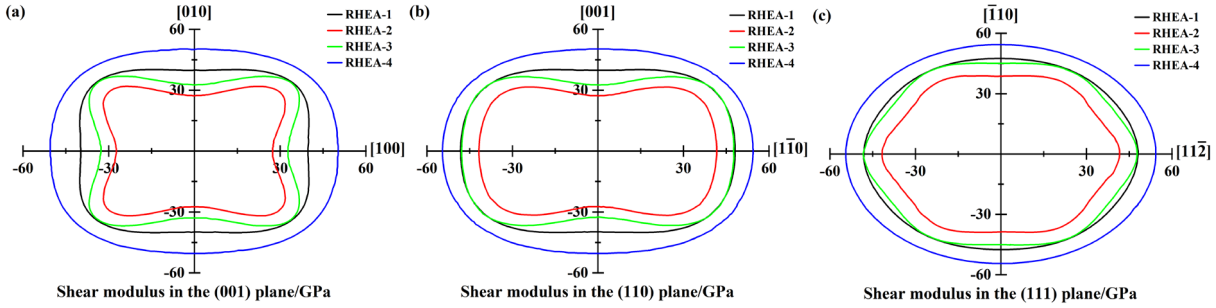

Figure S3. Projection curves of the 3D shear modulus anisotropic surfaces for four RHEAs on different crystal planes: (a) (001), (b) (110), and (c) (111).

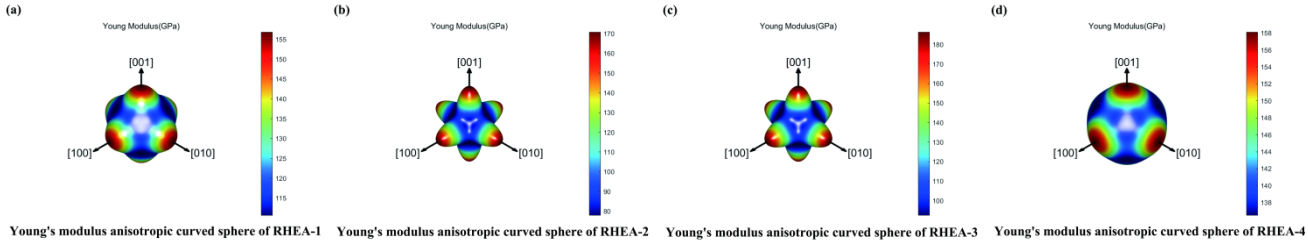

Figure S4. Anisotropic 3D surface of Young's modulus (*Y*) for RHEAs: (a) RHEA−1; (b) RHEA−2; (c) RHEA−3; (d) RHEA−4.

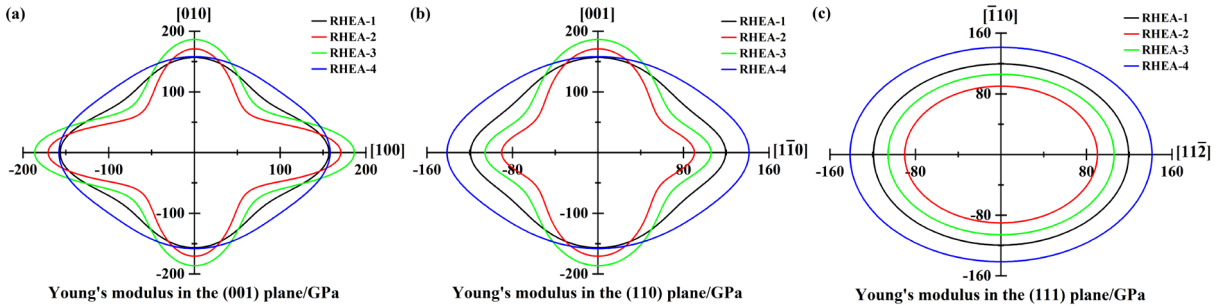

Figure S5. Projection curves of the 3D Young's modulus anisotropic surfaces for four RHEAs on different crystal planes: (a) (001), (b) (110), and (c) (111).

$$\begin{cases} \dfrac{1}{Y_{hkl}} = S_{11} - 2S_0 \dfrac{(hk)^2 + (hl)^2 + (lk)^2}{h^2 + k^2 + l^2} \\ S_0 = (2S_{11} - 2S_{12} - S_{44})/2 \end{cases} \quad \text{(S12)}$$

In the formula, S_{11}, S_{12}, and S_{44} are the elastic flexibility coefficients S_{ij} of the cubic RHEAs, and they are inverse matrices of the elastic stiffness coefficients C_{ij}, i.e., $S_{ij} = [C_{ij}]^{-1}$, with units of 1/GPa[50].

$$v(hkl,\theta) = \left\{ S_{12} + \frac{S_0}{h^2 + k^2 + l^2} \times \left[\left(\frac{h^2 l}{\sqrt{h^2 + k^2}\sqrt{h^2 + k^2 + l^2}} \cos\theta - \frac{hk}{\sqrt{h^2 + k^2}} \sin\theta \right) \right. \right.$$
$$+ \left(\frac{k^2 l}{\sqrt{h^2 + k^2}\sqrt{h^2 + k^2 + l^2}} \cos\theta - \frac{hk}{\sqrt{h^2 + k^2}} \sin\theta \right)^2 \quad \text{(S13) [50]}$$
$$\left. \left. + \frac{l\sqrt{h^2 + k^2}}{\sqrt{h^2 + k^2 + l^2}} \cos\theta \right] \right\} \Bigg/ \left[-S_{11} + 2S_0 \frac{(hk)^2 + (hl)^2 + (lk)^2}{h^2 + k^2 + l^2} \right]$$

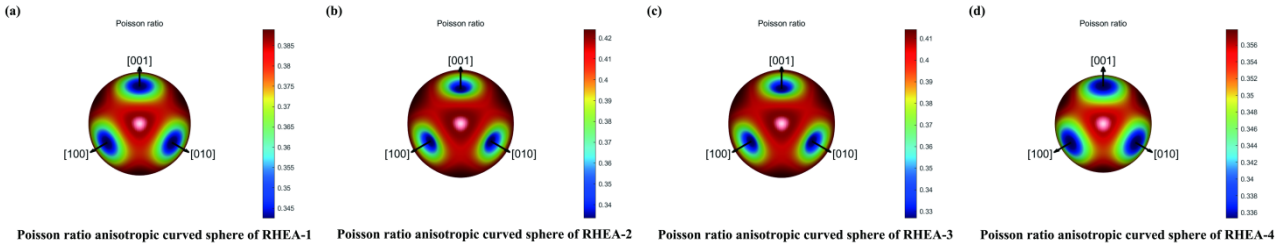

Figure S6. Anisotropic 3D surface of Poisson's ratio for RHEAs: (a) RHEA−1; (b) RHEA−2; (c) RHEA−3; (d) RHEA−4.

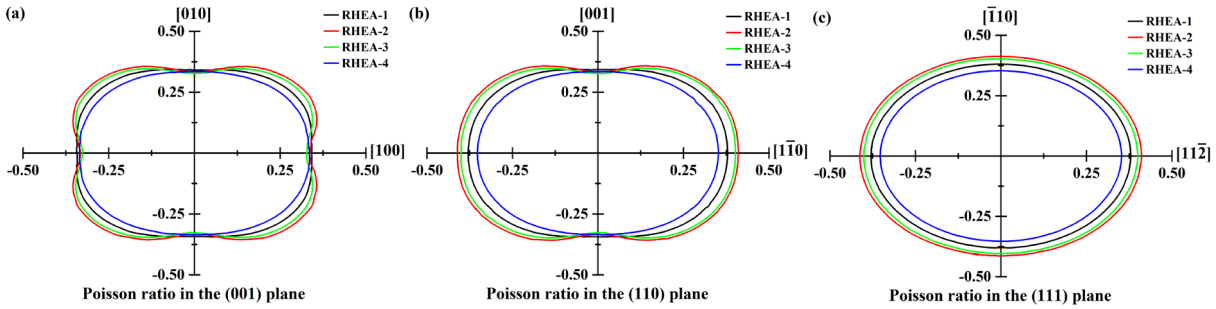

Figure S7. Projection curves of the 3D Poisson's ratio anisotropic surfaces for four RHEAs on different crystal planes: (a) (001), (b) (110), and (c) (111).



Figure S8. TC4 alloy substrate and preset powder.