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ARTICLE

Valence Electron Structure Parameter Analysis on Effect of Alloying Elements on Phase Transformation Temperature of Zirconium Alloys

Li Fei, Lin Cheng, Shi Yanhua, Liang Ping

School of Mechanical Engineering, Liaoning Petrochemical University, Fushun 113001, China

Abstract: According to the self-consistent bond length difference (SCBLD) method based on the empirical electron theory of solids and molecules, namely the Yu Ruihuang electron theory, the valence electron structure parameters (VESPs) were calculated to characterize the properties of alloy phases, and to investigate the influence of alloying elements (Al, Sn, Ti, Hf, V, Mo, Nb, Cu, Fe, Cr, Ni, Pd, and Re) on the phase transformation temperature of zirconium alloys. The results show that the sum of cohesive energy ($\sum \bar{E}'_C$) and the cohesive energy difference ($\Delta\bar{E}'_C$) of α and β phases can be used to characterize the effect of alloying elements on the phase transformation temperature of zirconium alloys. After dissolution into the zirconium matrix, the alloying elements (Cr, Al, Sn, Fe, Cu, Ni, and Ti) with smaller $\sum \bar{E}'_C$ can inhibit the $\alpha\rightarrow\beta$ phase transformation and increase the phase transformation temperature. However, the elements dissolved into the zirconium matrix, such as Hf, V, Mo, Pd, Nb, and Re, can promote the $\alpha\rightarrow\beta$ phase transformation and reduce the phase transformation temperature because of the larger $\sum \bar{E}'_C$. In the phase transformation process of zirconium alloys, the element (Al) with positive $\Delta\bar{E}'_C$ accelerates the $\beta\rightarrow\alpha$ phase transformation and increases the phase transformation temperature; the elements (Cr, Sn, Fe, Cu, Ni, Ti, Hf, V, Mo, Pd, Nb, and Re) with negative $\Delta\bar{E}'_C$ hinders the $\beta\rightarrow\alpha$ phase transformation and decreases the phase transformation temperature. The α-stabilizers (Al) and the β-stabilizers (Mo, Nb, Re, V, Pd) can be explained by both the $\sum \bar{E}'_C$ and $\Delta\bar{E}'_C$, whereas the β-stabilizers (Cr, Fe, Cu, Ni, and Ti) can only be explained by $\Delta\bar{E}'_C$. In addition, the α-stabilizers (Sn and Hf) can only be explained by $\sum \bar{E}'_C$.

Key words: zirconium alloy; phase transformation; electron structure; valence electron structure parameter; thermodynamics

Zirconium alloys have been widely used in nuclear fuel cladding tubes and structural materials due to their low neutron absorption and excellent corrosion resistance[1,2]. However, the mechanical properties of zirconium alloys (strength and wear resistance) usually cannot meet the practical application demands[3]. Therefore, many researchers try to optimize the mechanical properties of zirconium alloys by various methods[4], among which the alloying is considered as one of the most promising approaches, because the addition of alloying elements results in different phase transformation processes of zirconium alloys[5]. As a result, the microstructure and mechanical properties of zirconium alloys are optimized. Thus, it is of great significance to study the influence of alloying elements on the phase transformation of zirconium alloys.

There are generally two categories of the alloying method: α-stabilizers for increase in the phase transformation temperature and β-stabilizers for decrease in the phase transformation temperature[6,7]. Liang et al[8] investigated the effect of Al content on the properties of ZrTiAlV alloys, and found that the phase transformation temperature is increased with increasing the Al content. Qiu et al[9] studied the influence of Sn content on the phase transformation temperature of Zr-Sn-Nb-Fe alloys and found that the phase transformation temperature of $\alpha\rightarrow\alpha+\beta$ is increased with increasing the Sn content. Zhao et al[10] found that the addition of Nb reduces the

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Corresponding author: Lin Cheng, Ph. D., Professor, School of Mechanical Engineering, Liaoning Petrochemical University, Fushun 113001, P. R. China, Tel: 0086-24-56865042, E-mail: Cheng_lin1979@163.com

$\alpha \rightarrow \beta$ transformation temperature of N18 and N36 alloys. Canay et al[11] concluded that the Fe addition in Zr-Nb-Sn alloys decreases the $\alpha \rightarrow \beta$ phase transformation temperature. Ref. [9, 12-15] show that the addition of alloying elements (Cu, Cr, Mo, V, and Ti) into zirconium alloys can reduce the $\alpha \rightarrow \beta$ phase transformation temperature and stabilize the β phase. Although the influence of alloying elements on the phase transformation temperature of zirconium alloys has been widely studied and the general understanding based on the experiment results is obtained, the decomposition and reconstruction of phase structure units formed in solid solutions are still not clear. Therefore, it is necessary to understand the influence mechanism of alloying elements on the $\alpha \leftrightarrow \beta$ transformation in zirconium alloys at atom or electron structure level.

Although the first principle has been widely used to study the behavior of zirconium alloys, those investigations mainly focus on the precipitation of the second phase particles, diffusion behavior, strengthening mechanism, and corrosion behavior of zirconium alloys[16-20]. However, the effect of alloying elements on the phase transformation temperature of zirconium alloys is unclear, because the position and number of alloying atoms are uncertain in the alloying solid solutions of α and β phases. Even though the empirical electron theory of solids and molecules, namely Yu Ruihuang electron theory[21,22], can effectively solve the uncertainty problem in the modeling of alloy solid solutions, the theoretical modeling for alloying solid solutions still has many difficulties. The Yu Ruihuang electron theory has been widely used in many fields, such as alloying solid solutions[23], compounds[24], interfaces[25], magnetism[26], phase transformation[23,27,28], and strengthening mechanism[29], but it is rarely used to study the phase transformation of zirconium alloys.

In this research, the Yu Ruihuang electron theory was used to discuss the influence of alloying elements (Al, Sn, Hf, V, Fe, Cr, Cu, Mn, Ni, Pd, Nb, Ti, and Re) on the $\alpha \leftrightarrow \beta$ phase transformation mechanism of zirconium alloys at electronic structure level, providing a theoretical basis for the design and production of zirconium alloys.

1 Model Establishment and Results

1.1 Model establishment

The allotropy transformation temperature of pure zirconium is 863 °C, above which the pure zirconium has the body-centered cubic (bcc) structure. Otherwise, the pure zirconium shows the hexagonal close-packed (hcp) structure. When the alloying atom M is dissolved into the zirconium matrix, the binary α or β solid solution of Zr-M alloy is formed. In the solid solution of Zr-M alloy, α phase consists of pure α-Zr and α-Zr-M structure units; β phase consists of β-Zr and β-Zr-M structure units. When the alloying atoms are dissolved in the solid solutions and the atom positions are randomly and difficultly ascertained, it is assumed that only a fixed number of alloying M atoms are dissolved in one crystal cell of α and β phases based on the "segregation+average atom" model[28]. Thus, Fig. 1 shows different crystal cell models of α and β phases in zirconium alloys with and without alloying atoms M. After the alloying atoms M are dissolved into the crystal cells, the atoms at the lattice point become an imaginary mixed atom X, and the characteristic parameters of the mixed atom X can be expressed as follows:

$$\mathrm{ACP}(X) = x\mathrm{ACP}(M) + (1-x)\mathrm{ACP}(\mathrm{Zr}) \tag{1}$$

where ACP represents the atomic characteristic parameters in Yu Ruihuang electron theory, including the single bond radius (SBR) $R(1)$, covalent electron number n_C, lattice electron number n_l, magnetic electron number n_m, dumb pair electron number n_d, bond-forming ability f, and shielding factor b; x is the percentage of M atoms occupying the Zr lattices, and x=1/6 and 1/4 for α and β phases, respectively.

1.2 Results

Based on the crystal cell models in Fig. 1, the valence electron structure parameters (VESPs) calculated by the Yu Ruihuang electron theory can be obtained for α-Zr, α-Zr-M, β-Zr, and β-Zr-M phase structure units. Table 1 shows the names of covalent bonding (CBNs), lengths of experimental bonding (EBLs), equivalent bonding numbers (EBNs), and electron conservation equations (ECEs) required for the Yu Ruihuang electron theory calculation, i. e., the related parameters of structure units for bond length difference (BLD) and self-consistent bond length difference (SCBLD) calculation are listed.

By substituting the model parameters in Table 1 and the experimental lattice constants of the crystal cells into SCBLD calculation formulae[28,30], both the optimized lattice constants of α and β phases in zirconium alloys and the parameter β in Yu Ruihuang electron theory can be obtained, as shown in

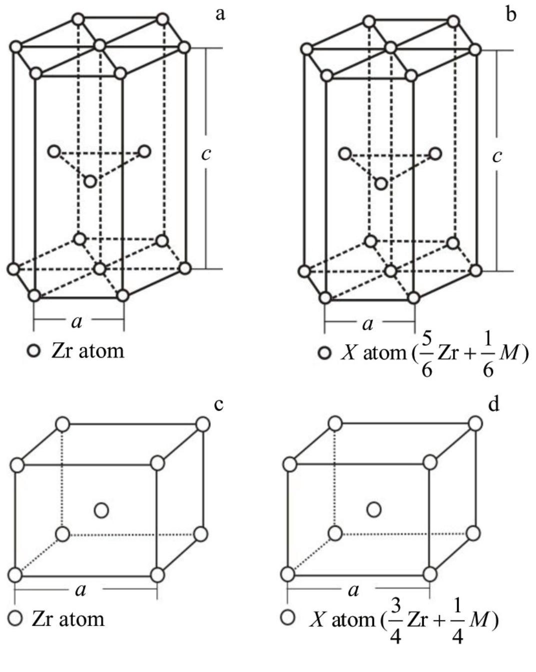

Fig.1 Crystal cell models of α and β phases in zirconium alloys without (a, c) and with (b, d) alloying atoms M: (a) α-Zr cell; (b) α-Zr-M cell; (c) β-Zr cell; (d) β-Zr-M cell

Table 1 Calculation parameters of structure units for BLD and SCBLD calculations

Structure unit	CBN	EBL	EBN, I_α	ECE
α-Zr	$D_{n\mathrm{A}}^{\mathrm{Zr-Zr}}$	$\sqrt{c^2/4+a^2/3}$	I_A=1×6×1=6	$\sum n_\mathrm{C}=n_\mathrm{C}^{\mathrm{Zr}}$
	$D_{n\mathrm{B}}^{\mathrm{Zr-Zr}}$	a	I_B=1×6×1=6	
	$D_{n\mathrm{C}}^{\mathrm{Zr-Zr}}$	$\sqrt{c^2/4+4a^2/3}$	I_C=1×6×1=6	
	$D_{n\mathrm{D}}^{\mathrm{Zr-Zr}}$	c	I_D=1×2×1=2	
	$D_{n\mathrm{E}}^{\mathrm{Zr-Zr}}$	$\sqrt{3}\,a$	I_E=1×6×1=6	
	$D_{n\mathrm{F}}^{\mathrm{Zr-Zr}}$	$\sqrt{c^2/4+7a^2/3}$	I_F=1×6×1=6	
α-Zr-M	$D_{n\mathrm{A}}^{X-X}$	$\sqrt{c^2/4+a^2/3}$	I_A=1×6×1=6	$\sum n_\mathrm{C}=n_\mathrm{C}^{X}$
	$D_{n\mathrm{B}}^{X-X}$	a	I_B=1×6×1=6	
	$D_{n\mathrm{C}}^{X-X}$	$\sqrt{c^2/4+4a^2/3}$	I_C=1×6×1=6	
	$D_{n\mathrm{D}}^{X-X}$	c	I_D=1×2×1=2	
	$D_{n\mathrm{E}}^{X-X}$	$\sqrt{3}\,a$	I_E=1×6×1=6	
	$D_{n\mathrm{F}}^{X-X}$	$\sqrt{c^2/4+7a^2/3}$	I_F=1×6×1=6	
β-Zr	$D_{n\mathrm{A}}^{\mathrm{Zr-Zr}}$	$\sqrt{3}\,a/2$	I_A=1×8×1=8	$\sum n_\mathrm{C}=n_\mathrm{C}^{\mathrm{Zr}}$
	$D_{n\mathrm{B}}^{\mathrm{Zr-Zr}}$	a	I_B=1×6×1=6	
β-Zr-M	$D_{n\mathrm{A}}^{X-X}$	$\sqrt{3}\,a/2$	I_A=1×8×1=8	$\sum n_\mathrm{C}=n_\mathrm{C}^{X}$
	$D_{n\mathrm{B}}^{X-X}$	a	I_B=1×6×1=6	

Table 2 and Table 3, respectively. Then the optimized lattice constants and parameter β are substituted into the BLD calculation to obtain the VESPs of α and β phases in zirconium alloys. Table 4 shows the detailed VESPs of non-negligible covalent bonding in α-Zr phase; Table 5 and Table 6 show the key VESPs in α and β phases, respectively. The meaning of VESPs in Table 4~6 is shown in Ref.[22,23,27,28,30,31], and VESPs with the prime-and-dot notation represent the statistical values of the corresponding parameters. The subscripts in Table 2~8 denote the hybrid states of atoms.

The cohesive energy ($\bar{E}'_\mathrm{C}$) of α and β phases in zirconium alloys can also be obtained by substituting the optimized lattice constants and parameter β into the calculation formula of crystal cohesive energy in Ref. [31]. The calculated cohesive energies of α and β phases are shown in Fig. 2 and the relevant parameters (P, Z) are listed in Table 7 and Table 8.

2 Discussion

According to Yu Ruihuang electron theory, the number of shared electrons pair (n'_A) and bonding energy (E'_A) of the strongest covalent bonding in the phase are usually used to characterize the interatomic bonding ability in the phase structure. The larger n'_A and E'_A suggest that the phase can be decomposed or reconstructed more difficultly because of the stronger interatomic bonding ability. Obviously, the elements preventing the bonding of α (or β) phase from decomposition or reconstruction hinder the $\alpha\leftrightarrow\beta$ phase transformation and therefore produce hysteresis effect. Thus, the phase transformation temperature is reduced or increased because the stabilization effect of β or α phase occurs, respectively.

Table 2 Lattice constants of α phase and parameter β with different alloying elements (nm)

Structure unit	a		c		β
	Calculated	Initial	Calculated	Initial	
α-Zr$_{\text{-B}}$	0.323 07	0.323 12	0.514 72	0.514 77	0.071
α-Zr$_{\text{-B}}$-Al	0.323 06	0.323 12	0.514 71	0.514 77	0.071
α-Zr$_{\text{-B}}$-Sn	0.323 54	0.323 12	0.515 19	0.514 77	0.071
α-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0.322 89	0.323 12	0.514 54	0.514 77	0.071
α-Zr$_{\text{-B}}$-Hf$_{\text{-B}}$	0.327 62	0.323 12	0.519 27	0.514 77	0.071
α-Zr$_{\text{-B}}$-V$_{\text{-AB}}$	0.324 86	0.323 12	0.516 51	0.514 77	0.071
α-Zr$_{\text{-B}}$-Mo$_{\text{-C}}$	0.324 82	0.323 12	0.516 47	0.514 77	0.071
α-Zr$_{\text{-B}}$-Nb$_{\text{-AB}}$	0.327 33	0.323 12	0.518 98	0.514 77	0.071
α-Zr$_{\text{-B}}$-Cu$_{\text{-A}}$	0.325 35	0.323 12	0.517 00	0.514 77	0.071
α-Zr$_{\text{-B}}$-Fe$_{\text{-AA}}$	0.326 17	0.323 12	0.517 82	0.514 77	0.071
α-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0.320 98	0.323 12	0.512 63	0.514 77	0.071
α-Zr$_{\text{-B}}$-Ni$_{\text{-AA}}$	0.325 14	0.323 12	0.516 79	0.514 77	0.071
α-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0.320 90	0.323 12	0.512 55	0.514 77	0.071
α-Zr$_{\text{-B}}$-Re	0.323 07	0.323 12	0.514 72	0.514 77	0.071

Table 3 Lattice constants of β phase and parameter β with different alloying elements (nm)

Structure unit	Calculated	Initial	β
β-Zr$_{\text{-A}}$	0.361 35	0.361 00	0.071
β-Zr$_{\text{-A}}$-Al	0.359 45	0.361 00	0.071
β-Zr$_{\text{-A}}$-Sn	0.360 12	0.361 00	0.071
β-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0.360 66	0.361 00	0.071
β-Zr$_{\text{-A}}$-Hf$_{\text{-A}}$	0.360 78	0.361 00	0.071
β-Zr$_{\text{-B}}$-V$_{\text{-AA}}$	0.359 61	0.361 00	0.071
β-Zr$_{\text{-B}}$-Mo$_{\text{-B}}$	0.363 91	0.361 00	0.071
β-Zr$_{\text{-B}}$-Nb$_{\text{-B}}$	0.362 41	0.361 00	0.071
β-Zr$_{\text{-B}}$-Cu$_{\text{-B}}$	0.362 23	0.361 00	0.071
β-Zr$_{\text{-B}}$-Fe$_{\text{-BA}}$	0.361 02	0.361 00	0.071
β-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0.360 13	0.361 00	0.071
β-Zr$_{\text{-B}}$-Ni$_{\text{-B}}$	0.357 57	0.361 00	0.071
β-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0.364 02	0.361 00	0.071
β-Zr$_{\text{-B}}$-Re	0.363 53	0.361 00	0.071

Table 4 VESPs of α-Zr phase

$R'(1)$=0.140 53 nm; n'_C=3.381 30; n'_l=0.618 70; n'_T=4.000 00						
CBN	EBN	EBL/nm	STBL/nm	n'_α	E'_C/kJ·mol^{-1}	$\Delta D'_{n\alpha}$/nm
$D_{n\mathrm{A}}^{\mathrm{Zr-Zr}}$	6	0.317 85	0.317 85	0.303 32	52.422 65	0.000 32
$D_{n\mathrm{B}}^{\mathrm{Zr-Zr}}$	6	0.323 07	0.323 07	0.256 05	43.536 09	0.000 32
$D_{n\mathrm{C}}^{\mathrm{Zr-Zr}}$	6	0.453 21	0.453 21	0.003 76	0.455 91	0.000 32
$D_{n\mathrm{D}}^{\mathrm{Zr-Zr}}$	2	0.514 72	0.514 72	0.000 51	0.054 61	0.000 32
$D_{n\mathrm{E}}^{\mathrm{Zr-Zr}}$	6	0.559 57	0.559 57	0.000 12	0.011 73	0.000 32
$D_{n\mathrm{F}}^{\mathrm{Zr-Zr}}$	6	0.556 57	0.556 57	0.000 13	0.013 00	0.000 32
$\Sigma I_\alpha r_\alpha$=11.147 55; β=0.071 nm; σ_N=2						

As shown in Table 5 and Table 6, when alloying elements (V, Mo, Nb, Cu, Ni, Pd, and Re) are dissolved into the α-Zr matrix, n'_A of α phase is increased. However, as the alloying

Table 5 VESPs of α phase with different alloying elements

Structure unit	n'_{A}	E'_{A}/kJ·mol^{-1}	$R'(1)$	n'_{C}	n'_{l}	n'_{T}	$\Sigma I_{\alpha} r_{\alpha}$	σ_{N}
α-Zr$_{\text{-B}}$	0.303 32	52.422 65	0.140 53	3.381 30	0.618 70	4.000 00	11.147 55	2
α-Zr$_{\text{-B}}$-Al	0.274 91	42.478 83	0.139 00	3.064 73	0.768 60	3.833 33	11.148 20	11
α-Zr$_{\text{-B}}$-Sn	0.298 16	44.955 78	0.140 43	3.317 75	0.682 25	4.000 00	11.127 25	12
α-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0.296 30	48.674 15	0.140 10	3.305 38	0.694 62	4.000 00	11.155 47	43
α-Zr$_{\text{-B}}$-Hf$_{\text{-B}}$	0.303 14	52.102 31	0.142 21	3.320 53	0.679 47	4.000 00	10.953 72	42
α-Zr$_{\text{-B}}$-V$_{\text{-AB}}$	0.312 91	50.306 55	0.141 68	3.464 05	0.702 62	4.166 67	11.070 33	42
α-Zr$_{\text{-B}}$-Mo$_{\text{-C}}$	0.311 51	50.112 80	0.141 59	3.449 13	0.777 35	4.226 48	11.072 12	57
α-Zr$_{\text{-B}}$-Nb$_{\text{-AB}}$	0.320 13	53.060 67	0.142 95	3.510 57	0.656 09	4.166 66	10.965 96	35
α-Zr$_{\text{-B}}$-Cu$_{\text{-A}}$	0.313 36	44.969 20	0.141 87	3.462 41	0.867 27	4.329 68	11.049 42	71
α-Zr$_{\text{-B}}$-Fe$_{\text{-AA}}$	0.302 09	43.849 19	0.141 61	3.327 43	0.916 28	4.243 71	11.014 62	73
α-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0.252 94	37.177 41	0.136 95	2.842 95	1.207 73	4.050 68	11.239 47	37
α-Zr$_{\text{-B}}$-Ni$_{\text{-AA}}$	0.326 78	46.268 94	0.142 44	3.613 67	0.796 40	4.410 07	11.058 28	67
α-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0.339 10	51.710 50	0.141 43	3.812 43	0.682 08	4.494 51	11.242 83	40
α-Zr$_{\text{-B}}$-Re	0.327 03	53.244 09	0.141 68	3.645 55	0.710 04	4.355 59	11.147 55	46

Table 6 VESPs of β phase with different alloying elements

Structure unit	n'_{A}	E'_{A}/kJ·mol^{-1}	$R'(1)$	n'_{C}	n'_{l}	n'_{T}	$\Sigma I_{\alpha} r_{\alpha}$	σ_{N}
β-Zr$_{\text{-A}}$	0.312 73	52.029 40	0.138 54	2.892 15	1.107 85	4.000 00	9.248 22	2
β-Zr$_{\text{-A}}$-Al	0.273 90	39.257 29	0.135 64	2.535 97	1.214 03	3.750 00	9.258 59	13
β-Zr$_{\text{-A}}$-Sn	0.324 05	44.775 00	0.138 54	2.999 04	1.000 96	4.000 00	9.254 95	14
β-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0.352 47	56.664 93	0.140 09	3.261 05	0.738 95	4.000 00	9.252 10	65
β-Zr$_{\text{-A}}$-Hf$_{\text{-A}}$	0.310 68	53.132 29	0.138 19	2.874 17	1.125 83	4.000 00	9.251 34	43
β-Zr$_{\text{-B}}$-V$_{\text{-AA}}$	0.362 44	56.528 77	0.140 07	3.355 35	0.894 65	4.250 00	9.257 71	59
β-Zr$_{\text{-B}}$-Mo$_{\text{-B}}$	0.369 04	58.363 83	0.142 21	3.407 85	0.925 50	4.333 35	9.234 42	57
β-Zr$_{\text{-B}}$-Nb$_{\text{-B}}$	0.376 24	61.283 75	0.141 86	3.477 38	0.772 62	4.250 00	9.242 51	73
β-Zr$_{\text{-B}}$-Cu$_{\text{-B}}$	0.392 35	51.426 12	0.142 42	3.626 63	0.969 79	4.596 42	9.243 45	93
β-Zr$_{\text{-B}}$-Fe$_{\text{-BA}}$	0.356 18	49.799 90	0.140 38	3.294 64	1.029 43	4.324 07	9.250 04	86
β-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0.296 98	40.975 84	0.137 22	2.748 52	1.346 35	4.094 87	9.254 90	48
β-Zr$_{\text{-B}}$-Ni$_{\text{-B}}$	0.413 47	54.687 33	0.141 19	3.832 44	0.846 60	4.679 04	9.268 88	83
β-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0.427 87	59.129 74	0.144 51	3.950 92	0.797 15	4.748 07	9.233 86	77
β-Zr$_{\text{-B}}$-Re	0.400 08	62.582 10	0.143 26	3.695 33	0.799 31	4.494 64	9.236 48	72

elements (Al, Sn, Ti, Hf, Fe, and Cr) are dissolved into the α-Zr matrix, n'_{A} of α phase is decreased. For β phase, the addition of alloying elements (Sn, Ti, V, Mo, Nb, Cu, Fe, Ni, Pd, and Re) causes the increase in n'_{A}; while the alloying elements (Al, Hf, and Cr) cause the decrease in n'_{A}. Therefore, the role of α-stabilizers (Al, Sn, and Hf) and β-stabilizers (Ti, V, Mo, Nb, Cu, Fe, Cr, Ni, Pd, and Re) in the phase transformation of zirconium alloys cannot be exactly explained by n'_{A}. The variation of E'_{A} for different structure units in Table 5 and Table 6 has the similar circumstance. Therefore, the effect of alloying elements on the phase transformation temperature of zirconium alloys is considered to use the cohesive energy ($\bar{E}'_{\text{C}}$) for explanation in this research.

It can be seen from Fig.2a that when the alloying atoms are dissolved into α-Zr matrix, all the alloying elements can result in the decreased cohesive energies of α-Zr matrix, except for Re element. However, the addition of Ni, Hf, Ti, V, Pd, Mo, Nb, and Re elements into β phase can cause an increase in the cohesive energy; while other elements (Al, Cr, Sn, Fe, and Cu) causes a decrease in the cohesive energy, as shown in Fig. 2b. Based on the Yu Ruihuang electron theory, the cohesive energy ($\bar{E}'_{\text{C}}$) represents the released energy during the formation of solids from free atoms or the absorbed energy during the formation of free atoms from solids. It can be concluded that the alloying elements except for Re element are not α-stabilizers, because the Zr alloys with α-Zr-M ($M\neq$Re) structure unit have relatively small $\bar{E}'_{\text{C}}$. Similarly, the alloying elements except for Re element are either not β-stabilizers, because the Zr alloys with β-Zr-M ($M\neq$Re) structure unit also have relatively small $\bar{E}'_{\text{C}}$. Obviously, the contradictory conclusions obtained from the cohesive energies of α or β phase cannot be used to investigate the influence of alloying elements on the phase transformation temperature of

Table 7 Related calculation parameters for cohesive energies of α phase with different alloying elements

Structure unit	P		Z	
	Zr	M	Zr	M
α-Zr$_{\text{-B}}$	0	-	4	-
α-Zr$_{\text{-B}}$-Al	0	0	4	13
α-Zr$_{\text{-B}}$-Sn	0	0	4	14
α-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0	0	4	4
α-Zr$_{\text{-B}}$-Hf$_{\text{-B}}$	0	0	4	4
α-Zr$_{\text{-B}}$-V$_{\text{-AB}}$	0	6	4	5
α-Zr$_{\text{-B}}$-Mo$_{\text{-C}}$	0	5	4	6
α-Zr$_{\text{-B}}$-Nb$_{\text{-AB}}$	0	6	4	5
α-Zr$_{\text{-B}}$-Cu$_{\text{-A}}$	0	0	4	11
α-Zr$_{\text{-B}}$-Fe$_{\text{-AA}}$	0	3	4	8
α-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0	5	4	6
α-Zr$_{\text{-B}}$-Ni$_{\text{-AA}}$	0	1	4	10
α-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0	1	4	10
α-Zr$_{\text{-B}}$-Re	0	4	4	7

Table 8 Related calculation parameters for cohesive energies of β phase with different alloying elements

Structure unit	P		Z	
	Zr	M	Zr	M
β-Zr$_{\text{-A}}$	0	-	4	-
β-Zr$_{\text{-A}}$-Al	0	0	4	13
β-Zr$_{\text{-A}}$-Sn	0	0	4	14
β-Zr$_{\text{-B}}$-Ti$_{\text{-B}}$	0	0	4	4
β-Zr$_{\text{-A}}$-Hf$_{\text{-A}}$	0	0	4	4
β-Zr$_{\text{-B}}$-V$_{\text{-AA}}$	0	6	4	5
β-Zr$_{\text{-B}}$-Mo$_{\text{-B}}$	0	5	4	6
β-Zr$_{\text{-B}}$-Nb$_{\text{-B}}$	0	6	4	5
β-Zr$_{\text{-B}}$-Cu$_{\text{-B}}$	0	0	4	11
β-Zr$_{\text{-B}}$-Fe$_{\text{-BA}}$	0	3	4	8
β-Zr$_{\text{-A}}$-Cr$_{\text{-AA}}$	0	5	4	6
β-Zr$_{\text{-B}}$-Ni$_{\text{-B}}$	0	1	4	10
β-Zr$_{\text{-B}}$-Pd$_{\text{-B}}$	0	1	4	10
β-Zr$_{\text{-B}}$-Re	0	4	4	7

zirconium alloys.

During the phase transformation of β and α phases, the coexistence temperature of β and α phases can be associated with the mean atom distance of clutter atoms in the two-phase region. The higher the coexistence temperature, the larger the mean atomic distance of clutter atoms. As a result, the coexistence temperature of β and α phases can be characterized by the cohesive energy obtained from the Yu Ruihuang electron theory. Because the cohesive energy of clutter atoms in the two-phase region is difficultly obtained, the sum of cohesive energies of β and α phases ($\sum\bar{E}'_{\text{C}}$) are used to characterize the coexistence temperature of two-phase region, as follows:

$$\sum\bar{E}'_{\text{C}} = \bar{E}'_{\text{C}\alpha} + \bar{E}'_{\text{C}\beta} \tag{2}$$

where $\bar{E}'_{\text{C}\alpha}$ represents the cohesive energy of α phase in zirconium alloys; $\bar{E}'_{\text{C}\beta}$ represents cohesive energy of β phase in zirconium alloys. Moreover, the larger the $\sum\bar{E}'_{\text{C}}$, the smaller the coexistence temperature. Fig. 3 shows the sum of the cohesive energies of α and β phases in zirconium alloys (the sum of the cohesive energies of α and β phases in pure zirconium is used as the reference).

It can be seen from Fig.3 that the sum of cohesive energies of the structure units with the alloying elements of Cr, Al, Sn, Fe, Cu, Ni, and Ti is smaller than that in pure zirconium. Thus, it is deduced that the coexistence temperature of α and β phases for the structure units with these elements is higher than the phase transformation temperature of pure zirconium. The alloying elements of Cr, Al, Sn, Fe, Cu, Ni, and Ti should be α-stabilizers in zirconium alloys. On the contrary, the alloying elements, such as Hf, V, Mo, Pd, Nb, and Re, are β-stabilizers due to their larger sum of cohesive energies compared with reference value. However, this analysis result is inconsistent with the experiment results for some alloying elements, such as Cr, Fe, Cu, Ni, Ti, and Hf. The discrepancy is mainly due to the facts that the phase transformation between α and β phases not only results in the decomposition and construction of α and β phases, but also involves the motion of decomposed atoms. In fact, the motion of decomposed atoms causes the fluctuation of the $\alpha\leftrightarrow\beta$ phase transformation temperature. In Ref. [28], the cohesive energy differences between α and β phases ($\Delta\bar{E}'_{\text{C}}$) are used to characterize the atom motion during the phase transformation of α and β phases in titanium alloys, which can also be used

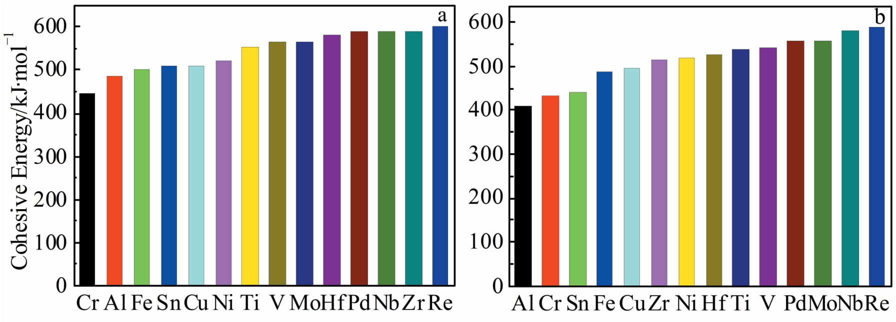

Fig.2 Cohesive energies of zirconium alloys with different alloying elements: (a) α-Zr-M and (b) β-Zr-M

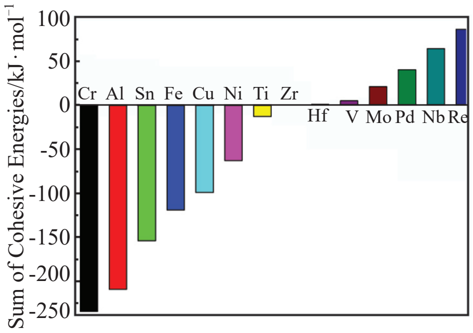

Fig.3 Sum of cohesive energies of α and β phases in zirconium alloys with different alloying elements

for Zr alloys as long as the expression of $\Delta\bar{E}'_{\mathrm{C}}$ is changed to $\Delta\bar{E}'_{\mathrm{C}}=\Delta\bar{E}_{\mathrm{C}\alpha}-\Delta\bar{E}_{\mathrm{C}\beta}$ or $\Delta\bar{E}'_{\mathrm{C}}=\Delta\bar{E}_{\mathrm{C}\beta}-\Delta\bar{E}_{\mathrm{C}\alpha}$ during the $\beta\rightarrow\alpha$ or $\alpha\rightarrow\beta$ phase transformations in this research.

Fig.4 shows the cohesive energy differences between α and β phases in zirconium alloys (the cohesive energy difference in pure zirconium is considered as the reference value). The cohesive energy difference of the structure units containing Al element exhibits the positive value during the phase transformation of from β to α; whereas that with other alloying elements all shows the negative cohesive energy difference. It is indicated that the positive cohesive energy difference is beneficial for the phase transformation from β to α, and thus the addition of Al element accelerates the phase transformation from β to α; while other elements hinder the phase transformation from β to α. As shown in Fig. 4b, the addition of Al element prevents the phase transformation from α to β; while other alloying elements accelerate the phase transformation from α to β. Based on the cohesive energy difference analysis, it can be deduced that the Al element is the α-stabilizer, and other elements are β-stabilizers. It is worth mentioning that the influence rules explained by $\sum\bar{E}'_{\mathrm{C}}$ and $\Delta\bar{E}'_{\mathrm{C}}$ are conflicting for some alloying elements, such as Sn, Cr, Fe, Cu, Ni, Ti, and Hf, during the $\alpha\leftrightarrow\beta$ phase transformation. After the comprehensive consideration, the alloying elements Cr, Fe, Cu, Ni, and Ti are regarded as β-stabilizers because their $\Delta\bar{E}'_{\mathrm{C}}$ is greater than their $\sum\bar{E}'_{\mathrm{C}}$; the elements Sn and Hf are considered as the α-stabilizers because the influence attributed to the sum of cohesive energy is superior to that of the cohesive energy difference.

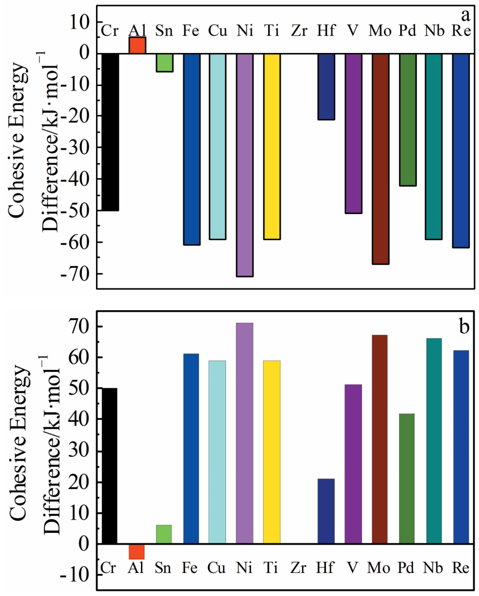

Fig.4 Cohesive energy differences of $\beta\rightarrow\alpha$ (a) and $\alpha\rightarrow\beta$ (b) phase transformations in zirconium alloys with different alloying elements

3 Conclusions

1) The sum of cohesive energies ($\sum\bar{E}'_{\mathrm{C}}$) of α and β phases in zirconium alloys can be used to characterize the coexistence temperature in the two-phase region, i. e., the smaller the $\sum\bar{E}'_{\mathrm{C}}$ of α and β phases, the higher the coexistence temperature of the two-phase region. The alloying elements of Cr, Al, Sn, Fe, Cu, Ni, and Ti with the relatively small value of $\sum\bar{E}'_{\mathrm{C}}$ of Zr alloys can increase the phase transformation temperature and promote the $\beta\rightarrow\alpha$ phase transformation. The Hf, V, Mo, Pd, Nb, and Re elements with relatively large $\sum\bar{E}'_{\mathrm{C}}$ of Zr alloys can decrease the phase transformation temperature and inhibit the $\beta\rightarrow\alpha$ phase transformation.

2) The cohesive energy difference ($\Delta\bar{E}'_{\mathrm{C}}$) between α and β phases in zirconium alloys can be used to characterize the atom motion during the phase transformation, and thus affect the fluctuation of phase transformation temperature. The addition of Al promotes the $\beta\rightarrow\alpha$ phase transformation or inhibits the $\alpha\rightarrow\beta$ phase transformation, and results in the increase in phase transformation temperature. However, other alloying elements of Cr, Sn, Fe, Cu, Ni, Ti, HF, V, Mo, Pd, Nb, and Re inhibit the $\beta\rightarrow\alpha$ phase transformation or promote the $\alpha\rightarrow\beta$ phase transformation, and result in the decrease in the phase transformation temperature.

3) Both the sum of cohesive energy and the cohesive energy difference can be used to explain the α-stabilizer of Al and the β-stabilizers of Mo, Nb, Re, V, Pd. But the β-stabilizers of Cr, Fe, Cu, Ni, and Ti are mainly explained by the cohesive energy difference. In addition, the α-stabilizers of Sn and Hf are mainly explained by the sum of cohesive energies.

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合金元素对锆合金相变温度影响的价电子结构参数分析

李　飞，林　成，史艳华，梁　平
(辽宁石油化工大学 机械工程学院，辽宁 抚顺 113001)

摘　要：基于固体与分子经验电子理论（余氏电子理论），采用自洽键距差法计算了表征合金相性质的价电子结构参数，并利用该参数讨论了合金元素（Al、Sn、Ti、Hf、V、Mo、Nb、Cu、Fe、Cr、Ni、Pd、Re等）对锆合金相变温度的影响。结果表明：合金元素对锆合金相变温度的影响可以用α和β相的结合能之和（$\sum\bar{E}'_C$）与结合能之差（$\Delta\bar{E}'_C$）来表征。溶入锆基体后结合能之和较小的Cr、Al、Sn、Fe、Cu、Ni、Ti等元素会抑制$\alpha\rightarrow\beta$相转变，提升相变温度；而溶入锆基体后结合能之和较大的Hf、V、Mo、Pd、Nb、Re等元素会促进$\alpha\rightarrow\beta$相转变，降低相变温度。在锆合金相变过程中，具有正结合能之差的元素（Al）将促进$\beta\rightarrow\alpha$相转变，提升相变温度；具有负结合能之差的元素（Cr、Sn、Fe、Cu、Ni、Ti、Hf、V、Mo、Pd、Nb、Re等）将抑制$\beta\rightarrow\alpha$相转变，降低相变温度。α相稳定元素（Al）和β相稳定元素（Mo、Nb、Re、V、Pd）可用$\sum\bar{E}'_C$和$\Delta\bar{E}'_C$来解释，但是β相稳定元素（Cr、Fe、Cu、Ni、Ti）主要通过$\Delta\bar{E}'_C$来解释；此外，α相稳定元素（Sn、Hf）可以用较小的$\sum\bar{E}'_C$来描述。

关键词：锆合金；相变；电子结构；价电子结构参数；热力学

作者简介：李　飞，男，1979年生，博士，副教授，辽宁石油化工大学机械工程学院，辽宁 抚顺 113001，电话：024-56865042，E-mail：lifei@lnpu.edu.cn