Mechanical properties of zirconium-based random alloys: alloying elements and composition dependencies

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Abstract

We present a detailed investigation on mechanical properties of Zr- X ($X = \text{Ti, Hf and Sc}$) alloy systems using the first-principles calculations in conjunction with special quasi-random structures (SQSs). It is found that the strength of mechanical coefficients such as elastic constants and elastic modulus depend linearly on the composition in Zr-Hf and Zr-Sc systems, whereas they depend parabolically on the composition in Zr-Ti system. Such a phenomenon is mainly induced by the presence of Zr- X metallic bond in the alloy systems. In addition, the strength of mechanical coefficients can be well described as a function of alloying composition by a special quadratic function that only has one coefficient F : $y = M_{\text{Zr}}(1-x) + M_X x + x(1-x)F$. With this function, mechanical coefficients of Zr- X alloy systems in whole composition range can be quickly estimated. Moreover Ti can considerably enhance the ductility of Zr when Ti concentration is 0.43.

Keywords: Zirconium, Alloys, Mechanical properties, Elastic constants, SQSs, First-principles calculations

1. Introduction

It is known that zirconium (Zr) and its alloys, possessing low thermal neutron absorption cross section and long-term dimensional stability under irradiation, have attracted great research interests[1, 2, 3]. For any structural material, the strength of mechanical coefficients are crucial parameters for their design and characterization. Experimental ways to obtain these mechanical coefficients are both lengthy and costly in some cases. Alternative ways are theoretical approaches such as the first-principles methods that are widely applied in ordered systems. However, the mechanical properties of the random system were rarely studied by the first-principles methods due to technical difficulties such as how to generate *ab initio* suitable structure models. The situation had a remarkable turn in 1990, when Zunger and his co-workers proposed a tractable approach on the basis of special quasi-random structures (SQSs) technique to describe random alloys by constructing a finite supercell to match as close as possible with the correlation functions of random alloy[4]. Compared with other commonly employed descriptions, such as the supercells, the cluster expansion (CE)

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and the coherent potential approximation (CPA) [5], the SQSs can significantly reduce computation time, acquire comparable accuracy and directly consider local environments. Therefore SQSs are widely used to investigate random alloys and have led to successful research outcomes[5, 6, 7, 8, 9, 10, 11, 12, 13].

It is too hard to investigate all composition points of Zr-based alloys either by experiments or by the first-principles methods. Thus establishing the relationship between composition and properties is rather important. In doing so, in the present study we intend investigating Zr-Ti (titanium), Zr-Hf (hafnium) and Zr-Sc (scandium) random alloy systems by using the first-principles methods in combination with special quasi-random structures. Choosing those alloying systems for this study is based on following facts. Firstly, being the neighbors of Zr in the periodic table of elements, the transition metals Ti, Hf and Sc have very similar chemical properties to Zr and all of them crystallize in hexagonal closed-packed (*hcp*) structure (α phase) at room temperature. Furthermore, Zr-Ti, Zr-Hf and Zr-Sc alloy systems are characterized by a full solubility of their constituents over a wide temperature range[14]. Hence, they are ideal systems to uncover the relationship. For each Zr- X system, we consider seven structures such as Zr_2 , $Zr_{15}X$, $Zr_{12}X_4$, Zr_8X_8 , Zr_4X_{12} , ZrX_{15} and X_2 . One of theoretical findings from this study is that the mechanical properties of Zr- X alloys are mainly determined by two factors, namely the alloying constituents and alloying effects. Moreover a mechanical coefficient can be well described via a functional form of alloying composition, given by a special quadratic function: $y = M_{Zr}(1 - x) + M_Xx + x(1 - x)F$. By employing this function, the ductility of Zr can be deduced and can be significantly enhanced through alloying with Ti. In such a case, the enhancement can reach up to a global maximum for Ti concentration at 0.43.

2. Theoretical Methods

2.1. Computational Details

Within the framework of density functional theory, the first-principles calculations code of VASP[15] (Vienna Ab *initio* Simulation Package) is employed to conduct all calculations in the present study. The exchange and correlation potentials are depicted by generalized gradient approximation (GGA)[16] of Perdew-Burke-Ernzerhof (PBE). The energy cutoff and k-mesh are chosen to balance accuracy against computational time. Here we use 300 eV as cutoff energy for all calculations, $(13 \times 13 \times 8)$ k-mesh for structures $Zr_{15}X$, Zr_8X_8 , ZrX_{15} , and $(25 \times 25 \times 17)$ k-mesh for Zr_2 as well as X_2 , and $(11 \times 13 \times 6)$ for structures $Zr_{12}X_4$ and Zr_4X_{12} . Elastic constants are calculated by stress-strain approach, *i.e.*, applying a number of strains and calculating corresponding stress, then obtaining elastic constants by solving generalized Hooke law. More details about this approach have been documented in the literature[17].

2.2. The SQS Template

The technique of SQSs was proposed by Zunger and his co-workers[4]. One of its major advantages is that this approach can considerably overcome the computational difficulties in modeling random alloys by constructing a finite supercell to mimic as close as possible to the correlation functions of a random alloy. The

correlation functions of a binary random alloy $A_{(1-x)}B_x$ are $\bar{\Pi}_{k,m,n} = (2x-1)^k$, where x is the concentration of element B , k is the number of vertices and m is the maximum distance spanned by the figure edge in units of nearest-neighbor shells. For *hcp* structure with an ideal c/a ratio, although the atom-pair (0,0,0) and (1,0,0) has the same interatomic distance with the atom-pair (0,0,0) and (1/3,2/3,1/2), they have different symmetry operations. In addition, the c/a ratio is not ideal for majority of hexagonal structures, leading to differences between these two pairs. Thus, the index n is employed to distinguish them. The correlation functions of SQSs are defined with the Ising model language and the details about this can be found in literatures[4, 5, 18, 19]. The quality of SQSs depends on how their correlation functions come up with the correlation functions of the random alloy.

2.3. Projection of Elastic Tensor to Those of Higher Symmetry

It is well known that the symmetry of an elastic tensor is controlled by atomic arrangements in microstructure. For example, [100] and [010] directions of *hcp* structures possess the same atomic arrangements, which leads to $C_{11} = C_{22}$. For *hcp* type of random alloys, [100] and [010] are not the exactly equivalent directions owing to random occupation of atoms in the lattice sites. However they still have the same average environments and are supposed to hold $C_{11} = C_{22}$, which means that the elastic tensors of random alloys own the same symmetry as those of ordered phase. Normally, the size of SQSs used to mimic random alloys is finite that leads to symmetrical directions having different average environments and introducing a part of symmetry deviations. In addition, the first-principles approach will also introduce some symmetry deviations. As a consequence, calculated elastic tensor having 21 independent components differs from the experimental one that only has 5 independent components. Rather than ignoring the extra 16 independent components, here we would like to introduce a projection technique that was proposed by Moakher *et al.*[20] to project calculated elastic tensor in order to have the same form as the experimental one. The key principle of this technique is using a series of point group operations in obtaining a higher symmetry elastic tensor from one with arbitrary symmetry. Technically, those point group operations are presented by projector P^{sym} . Here *hcp* type of projector P^{hcp} is employed,

$$P^{hcp} = \begin{pmatrix} Q^{hcp} & 0_{9 \times 12} \\ 0_{12 \times 9} & 0_{12 \times 12} \end{pmatrix}, \quad (1)$$

where Q^{hcp} is

$$\begin{pmatrix} 3/8 & 3/8 & 0 & 0 & 0 & 1/4\sqrt{2} & 0 & 0 & 1/4 \\ 3/8 & 3/8 & 0 & 0 & 0 & 1/4\sqrt{2} & 0 & 0 & 1/4 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/4\sqrt{2} & 1/4\sqrt{2} & 0 & 0 & 0 & 3/4 & 0 & 0 & -1/2\sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & 1/2 & 0 \\ 1/4 & 1/4 & 0 & 0 & 0 & -1/2\sqrt{2} & 0 & 0 & 1/2 \end{pmatrix}.$$

In order to carry out the projection, firstly, the elastic tensor should be written as a vector with 21 components, which reads

$$\begin{aligned} C = & (C_{11}, C_{22}, C_{33}, \sqrt{2}C_{23}, \sqrt{2}C_{13}, \sqrt{2}C_{12}, 2C_{44}, \\ & 2C_{55}, 2C_{66}, 2C_{14}, 2C_{25}, 2C_{36}, 2C_{34}, 2C_{15}, 2C_{26}, \\ & 2C_{24}, 2C_{35}, 2C_{16}, 2\sqrt{2}C_{56}, 2\sqrt{2}C_{46}, 2\sqrt{2}C_{45}), \end{aligned} \quad (2)$$

$$C^{hcp} = P^{hcp}C. \quad (3)$$

Here the numerical coefficients (2 and $\sqrt{2}$) are employed to ensure the invariance of the Euclidean norm[20]. Using equation (3), the projected elastic constants tensor C^{hcp} can be obtained as following,

$$\begin{aligned} C^{hcp} = & (\bar{C}_{11}, \bar{C}_{11}, \bar{C}_{33}, \sqrt{2}\bar{C}_{13}, \sqrt{2}\bar{C}_{13}, \sqrt{2}\bar{C}_{12}, 2\bar{C}_{44}, \\ & 2\bar{C}_{44}, \bar{C}_{11} - \bar{C}_{12}, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0), \end{aligned} \quad (4)$$

where projected elastic constants $\bar{C}_{11}$, $\bar{C}_{33}$, $\bar{C}_{44}$, $\bar{C}_{12}$, $\bar{C}_{13}$ are determined by following equations

$$\begin{aligned} \bar{C}_{11} &= 3(C_{11} + C_{22})/8 + C_{12}/4 + C_{66}/2, \bar{C}_{33} = C_{33}, \bar{C}_{44} = (C_{44} + C_{55})/2, \\ \bar{C}_{12} &= (C_{12} + C_{22})/8 + 3C_{12}/4 - C_{66}/2, \bar{C}_{13} = (C_{13} + C_{23})/2. \end{aligned} \quad (5)$$

The Euclidean distance deviations P [11] can be employed to characterize the degree of symmetry deviations, which is defined as

$$P = \|C - C^{hcp}\|/\|C\|. \quad (6)$$

For convenience, from now on all projected elastic constants $\bar{C}_{ij}$ will be denoted as C_{ij} and the unprojected elastic constants will not be mentioned any more.

3. Results and Discuss

The SQS approach has been widely employed to investigate thermodynamic properties of material systems such as[5, 7, 19, 21, 22]. There are already some SQSs templates with arbitrary supercell shape (*bcc*[5], *fcc*[22]

and *hcp*[18]) in the literatures. However, when SQS approach was employed to investigate elastic constants previously, SQSs were usually reconstructed[10, 12] in order to possess $A \times A \times A$ supercell shape because elastic constants are sensitive to the symmetry of the model[11]. In fact, SQSs employed to investigate elastic constants firstly should own acceptable correlation functions, and then should own $A \times A \times A$ supercell shape that is suggested but not obligatory. Based on this rule, two types of SQSs-16 (Fig. 1 and Table I) are generated for Zr-*X* alloys with the alloy theoretic automation toolkit (ATAT). The first one keeps a $2 \times 2 \times 2$ supercell, built for Zr_8X_8 , which balances the symmetry of the model to against the correlation functions. The another one, built for Zr_4X_{12} and Zr_{12}X_4 , does not keep a $2 \times 2 \times 2$ supercell in order to acquire the acceptable correlation functions. Its lattice vectors (*a*) can be linked with those of *hcp* unit cell (*c*) via an equation $a = bc$ where matrix *b* is given as

$$\begin{pmatrix} 1 & 0 & -1 \\ 1 & -2 & 0 \\ -3 & 0 & -1 \end{pmatrix}.$$

As a result, our SQSs applied in this study have following characteristics: (a) the comparable correlation functions among different concentrations, (b) $2 \times 2 \times 2$ supercell shape at concentration $x = 0.5$. Fig. 1(a) is the schematic diagram of Zr_{12}X_4 ($x = 0.25$) and Zr_4X_{12} ($x = 0.75$), and Fig. 1(b) is the schematic diagram of Zr_8X_8 ($x = 0.5$) where an orange plane and four blue planes are employed to divide it into 8 *hcp* unit cells. The lattice vectors and atomic sites of SQSs in fractional coordinates are given in Table I. Although the SQS at a concentration $x = 0.5$ possesses $2 \times 2 \times 2$ supercell shape, the correlation functions agree well with those reported by Shin *et al.* [18] (TableII). For our SQSs, the average two-body correlation functions of Zr_8X_8 equal to those of a random alloy from the first- to the fourth-nearest-neighbor, and the average three-body as well as the average four-body correlation functions equal to those of the third- and the second-nearest-neighbor respectively. The average two-body correlation functions of Zr_{12}X_4 (Zr_4X_{12}) equal to those of random alloy for pairs from the first- to the fourth-nearest-neighbor. These guarantee a high quality of SQS templates to mimic random alloys.

Based on above shown structures, mechanical properties of Zr-Ti, Zr-Hf and Zr-Sc alloy systems, such as, elastic constants, bulk modulus and shear modulus, are systematically investigated. Elastic constants, which can be directly calculated by the first-principles approach, are crucial mechanical parameters which link stress with strain. In addition, a number of properties can be derived from them. In the present work, we firstly calculate elastic tensor. Then by applying projection technique, calculated tensor is projected to satisfy *hcp* symmetry. Bulk modulus (*B*) and shear modulus (*G*) are obtained in terms of Voigt-Reuss-Hill approach[23]. The *B/G* rate and Poisson's ratio ν are also calculated to examine the ductility where we should notice that about 1.75[23] for *B/G* and 0.3 for ν are crucial points to separate ductile (*B/G* > 1.75 and ν > 0.3) and brittle materials (*B/G* < 1.75 and ν < 0.3).

The results for the elastic constants, bulk modulus (*B*), shear modulus (*G*), *B/G* and Poisson's ratio ν from the present study *vs* accessible experimental values and other theoretical data for pure metals are listed

Table 1: Lattice vectors and atomic positions of structures, which are given in their ideal, unrelaxed states

$Zr_{15}X_1$ (Zr_1X_{15})	$Zr_{12}X_4$ (Zr_4X_{12})	Zr_8X_8
lattice vectors	lattice vectors	lattice vectors
(6.510 0.000 0.000)	(3.255 0.000 -5.315)	(6.510 0.000 0.000)
(3.255 5.638 0.000)	(0.000 -5.638 0.000)	(3.255 5.638 0.000)
(0.000 0.000 10.631)	(-9.765 0.000 -5.315)	(0.000 0.000 10.631)
Atomic positions	Atomic positions	Atomic positions
A-(1 0 0)	A-(1/8 1/2 7/8)	A-(1 0 0)
A-(1/6 1/6 1/4)	A-(7/8 1/3 5/8)	A-(1/6 1/6 1/4)
A-(1/2 0 0)	A-(3/8 1/2 5/8)	A-(1/2 0 0)
A-(2/3 1/6 1/4)	A-(3/8 1/3 1/8)	A-(2/3 1/6 1/4)
A-(1/2 1/2 0)	A-(7/8 1/2 1/8)	A-(1/2 1/2 0)
A-(2/3 2/3 1/4)	A-(5/8 1/3 7/8)	A-(2/3 2/3 1/4)
A-(1 0 1/2)	A-(0 5/6 1/2)	A-(1 0 1/2)
A-(1/6 1/6 3/4)	A-(1/4 5/6 1/4)	A-(1/6 1/6 3/4)
A-(1/6 2/3 3/4)	A-(3/4 0 1/4)	B-(1/6 2/3 3/4)
A-(1 1/2 1/2)	A-(1/2 5/6 0)	B-(1 1/2 1/2)
A-(2/3 2/3 3/4)	A-(0 0 0)	B-(2/3 2/3 3/4)
A-(1 1/2 0)	A-(3/4 5/6 3/4)	B-(1/2 1/2 1/2)
A-(2/3 1/6 3/4)	B-(1/2 0 1/2)	B-(2/3 1/6 3/4)
A-(1/2 0 1/2)	B-(1/4 0 3/4)	B-(1/2 0 1/2)
A-(1/6 2/3 1/4)	B-(5/8 1/2 3/8)	B-(1/6 2/3 1/4)
B-(1/2 1/2 1/2)	B-(1/8 1/3 3/8)	B-(1 1/2 0)

Table 2: Pair and multi-site correlation functions of Zr_8X_8 and $Zr_{12}X_4$ configurations when the c/a ratio is ideal. The number in the square bracket next to $\bar{\Pi}_{k,m,n}$ is the degeneracy factor at the same distance with crystallographically equivalent.

	Zr_8X_8			$Zr_{12}X_4$ (Zr_4X_{12})		
	Random	Ref[18]	Present Work	Random	Ref[18]	Present Work
$\bar{\Pi}_{2,1,1}[6]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,1,2}[6]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,2,1}[6]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,3,1}[2]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,4,1}[12]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,4,2}[6]$	0.0000	0.0000	0.0000	0.2500	0.4583	0.3333
$\bar{\Pi}_{2,5,1}[12]$	0.0000	0.0000	-0.3333	0.2500	0.3333	0.4583
$\bar{\Pi}_{2,6,1}[6]$	0.0000	-0.3333	1.0000	0.2500	0.1667	0.1667
$\bar{\Pi}_{2,7,1}[12]$	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500
$\bar{\Pi}_{2,8,1}[12]$	0.0000	0.0000	-0.3333	0.2500	0.1667	0.1667
$\bar{\Pi}_{3,1,1}[12]$	0.0000	0.0000	0.0000	0.1250	-0.0833	-0.1667
$\bar{\Pi}_{3,1,2}[2]$	0.0000	0.0000	0.0000	0.1250	0.2500	-0.2500
$\bar{\Pi}_{3,1,3}[2]$	0.0000	0.0000	0.0000	0.1250	0.2500	-0.2500
$\bar{\Pi}_{3,2,1}[24]$	0.0000	0.0000	0.0000	0.1250	-0.042	-0.1250
$\bar{\Pi}_{3,3,1}[6]$	0.0000	0.0000	0.0000	0.1250	-0.0833	-0.0833
$\bar{\Pi}_{4,1,1}[4]$	0.0000	0.0000	0.0000	0.0625	-0.0833	0.2500
$\bar{\Pi}_{4,2,1}[12]$	0.0000	0.0000	0.0000	0.0625	-0.1667	0.1667
$\bar{\Pi}_{4,2,2}[12]$	0.0000	0.0000	0.0000	0.0625	0.0000	0.0000
$\bar{\Pi}_{4,3,1}[6]$	0.0000	0.3333	-0.3333	0.0625	-0.1667	0.0833

Table 3: Calculated elastic constants C_{11} , C_{33} , C_{12} , C_{13} , C_{44} , bulk modulus (B), shear modulus (G), Poisson's ratio (ν), B/G and euclidean distance deviations $P = ||C - C^{hcp}||/||C||$ for Zr-Ti, Zr-Hf, Zr-Sc random alloy systems. For comparison, accessible experimental and theoretical values are also listed.

	C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	B	G	ν	B/G	P
	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)			(%)
Zr	144.106	163.926	70.332	71.664	23.419	97.432	31.468	0.354	3.096	1.049
Zr (Theory)[23]	145.300	166.100	67.300	69.500	24.300	96.589	31.273	0.354	3.089	
Zr (Exp, 298K)[24]	143.400	164.800	72.800	65.300	32.000	95.378	35.747	0.333	2.668	
Zr ₁₅ Ti ₁	144.946	163.108	70.628	70.588	25.470	97.270	32.926	0.348	2.954	0.064
Zr ₁₂ Ti ₄	130.633	157.202	81.304	75.505	28.838	98.110	27.386	0.372	3.583	7.286
Zr ₈ Ti ₈	135.753	163.377	86.560	78.644	25.721	101.709	26.844	0.379	3.789	4.182
Zr ₄ Ti ₁₂	145.073	173.469	90.130	80.529	31.739	107.322	32.209	0.364	3.332	5.523
Zr ₁ Ti ₁₅	167.734	181.558	87.462	82.973	37.363	113.747	40.383	0.341	2.817	0.087
Ti	179.019	189.534	87.912	82.640	40.511	116.991	44.598	0.331	2.623	0.838
Ti (Theory)[23]	174.800	189.500	87.500	80.000	40.900	114.900	43.980	0.330	2.613	
Ti (Exp, 298K)[24]	162.400	180.700	92.000	69.000	46.700	107.278	46.387	0.311	2.313	
Zr ₁₅ Hf ₁	148.904	166.451	68.958	71.423	25.124	98.483	33.849	0.346	2.910	0.073
Zr ₁₂ Hf ₄	156.402	171.194	69.914	70.931	32.286	100.826	39.273	0.328	2.567	0.892
Zr ₈ Hf ₈	165.226	179.999	70.006	72.904	37.042	104.545	43.642	0.317	2.396	0.477
Zr ₄ Hf ₁₂	176.332	189.753	73.217	72.031	46.640	108.486	50.446	0.299	2.151	0.870
Zr ₁ Hf ₁₅	184.110	192.695	72.694	73.701	50.374	111.200	53.923	0.291	2.062	0.062
Hf	185.995	196.981	73.666	73.893	52.403	112.413	55.264	0.289	2.034	0.201
Hf (Theory)[23]	183.600	197.900	71.100	71.100	51.100	110.189	54.113	0.289	2.036	
Hf (Exp, 298K)[24]	188.100	196.900	77.200	66.100	55.700	110.211	57.667	0.277	1.911	
Zr ₁₅ Sc ₁	153.311	160.871	58.689	66.733	31.068	94.547	39.475	0.317	2.395	0.047
Zr ₁₂ Sc ₄	146.638	151.275	50.690	56.694	37.006	85.914	42.591	0.287	2.017	1.019
Zr ₈ Sc ₈	130.239	134.452	44.285	46.389	33.149	74.436	39.055	0.277	1.906	2.874
Zr ₄ Sc ₁₂	115.445	115.544	39.906	36.707	32.257	63.548	35.914	0.262	1.769	1.555
Zr ₁ Sc ₁₅	105.388	103.926	37.238	29.760	30.341	56.438	33.359	0.253	1.692	0.179
Sc	102.125	100.433	36.750	27.034	30.461	53.973	32.850	0.247	1.643	0.000
Sc (Theory)[23]	104.800	105.200	37.700	29.300	31.600	56.378	33.527	0.252	1.682

Figure 1: (Color online) Schematic diagrams of SQSSs-16, where red and green spheres represent Zr and X atoms, respectively. (a) for Zr_4X_{12} ($Zr_{12}X_4$) with $a=5.934\text{\AA}$, $b=5.535\text{\AA}$, $c=10.696\text{\AA}$, $\alpha = 89^\circ$, $\beta = 94^\circ$ and $\gamma = 90^\circ$ (b) for Zr_8X_8 with $2\times 2\times 2$ supercell shape ($a = b = 6.510\text{\AA}$, $c = 10.631\text{\AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, where an orange plane and four blue planes are employed to divide it into 8 *hcp* unit cell.

Figure 2: (Color online) Mechanical properties of Zr-Ti alloy system (a) C_{11} , (b) C_{33} , (c) C_{44} , (d) C_{12} , (e) C_{13} , (f) ν , (g) B , (h) G and (i) B/G . The red spots are calculated values and the black lines are fitting function $y = M_{Zr}(1-x) + M_Xx + x(1-x)F$ with parameter F .

in Table III, from where we can see that a good agreement between our results and those in the literature values can be found. For example, calculated C_{11} (144.106 GPa) for Zr_2 agrees well with the experimental datum (143.400 GPa). To the best of our knowledge, there are no experimental data for elastic constants in random alloys[10, 11, 12]. Although Hsueh-Chuan Hsu *et al.* has prepared a series of binary Zr-Ti alloys and

measured some of their mechanical properties such as hardness and bending moduli, elastic constants have not yet been measured experimentally [25]. Meanwhile, those Zr-Ti alloys were neither random nor single crystals. Their results showed that the bending moduli changed with varying Ti concentration. Nevertheless the variation tendency was undistinguishable due to experimental errors. Based on the calculated elastic constants, the mechanical stability can be judged according to Born's criteria. For a hexagonal system,

$$\begin{aligned} C_{11} - |C_{12}| &> 0 \\ (C_{11} + C_{12})C_{13} - 2C_{12}^2 &> 0 \\ C_{44} &> 0 \end{aligned} \quad (7)$$

It is clear that all of the Zr- X alloy systems are mechanically stable. The obtained B/G (last but one column in Table III) indicates that Zr-Ti and Zr-Hf are ductile materials. Although Sc is a brittle material, ScZr alloys are ductile materials when Zr concentration is great than 0.25.

To analyze the composition dependence, mechanical properties as a function of alloying concentration are fitted with a quadratic function which just has one parameter F ,

$$y = M_{Zr}(1 - x) + M_X x + x(1 - x)F, \quad (8)$$

where y is the mechanical property of $Zr_{(1-x)}X_x$ alloy, M_{Zr} is the mechanical property of Zr, M_X is the mechanical property of alloying elements X ($X = \text{Ti, Hf and Sc}$). The physical meaning of $M_{Zr}(1 - x)$ and $M_X x$ are the contribution to mechanical properties of $Zr_{(1-x)}X_x$ from pure Zr and pure X metal respectively. F is the contribution of interaction between a pair of Zr and X atoms to the mechanical properties of $Zr_{(1-x)}X_x$ and $x(1 - x)$ represents the number of pairs of Zr and X . Thus the physical meaning of $x(1 - x)F$ is the contribution from all of interactions between Zr and X to mechanical properties of $Zr_{1-x}X_x$. This function decomposed the strength of mechanical properties into two parts: the first one is determined by alloying constituents and the second one is determined by alloying effect. The results of fitting are shown in Fig. 2 and Fig.3, from where we can see that all mechanical properties change apparently with alloying concentration. Taking B/G rate for instance, it shows nonlinear dependence on alloying composition with a global maximum around Ti concentration at 0.43 in Zr-Ti alloy system (Fig. 2(i)), while it gradually decreases with increasing alloying elements in Zr-Hf (Fig. 3(a)) and Zr-Sc (Fig. 3(b)) systems.

The performance of Eq. (8) for Zr-Ti system is shown in Fig. 2. For elastic constants, C_{ii} exhibits concave curves, while C_{ij} ($i \neq j$) exhibits convex curves. B/G and ν reveal convex curves as well, which means that Zr alloying with Ti can significantly improve the ductility. By taking the first derivative of fitting function, the global maximum of B/G , where the enhancement of the ductility is the best, can be found. Here the fitting function for B/G is $y = 3.096(1 - x) + 2.623x + 3.29x(1 - x)$ and the global maximum is at $x = 0.43$. The first two terms, contribution from pure constituent, decrease with x , while the last term, contribution from alloying effects, firstly increases with $x \in (0, 0.5)$, and then decreases with $x \in (0.5, 1)$. As a result, the value of y firstly increases with $x \in (0, 0.43)$, and then decreases with $x \in (0.43, 1)$. This explains the fact

Figure 3: (Color online) Mechanical properties of Zr-Hf [(a), (c)] and Zr-Sc [(b), (d)] alloy systems. (a) and (b) are B/G , while (c) and (d) are bulk modulus. The red spots are calculated values and the black lines are fitting function $y = M_{Zr}(1-x) + M_X x + x(1-x)F$.

that y does not have mirror symmetry, which can be seen clearly from Fig.2(i). B/G in Zr-Hf system (Fig. 3(a)) and Zr-Sc system (Fig. 3(b)) gradually decreases with concentration indicating that the ductility of Zr cannot be improved by alloying with Sc or Hf.

While some of the mechanical properties have parabolic composition dependence (Fig. 2), some other mechanical properties have linear composition dependence (Fig. 3). This behavior is mainly induced by the mechanical properties of Zr- X metallic bond. There is only one type of metallic bond in pure metal Zr(Zr-Zr). When X is introduced as an alloy element in Zr, the second type of bond (Zr- X) is introduced. Normally, the mechanical properties of Zr- X bond are different from those of Zr-Zr or X - X bonds. Thus the mechanical properties of Zr- X alloys are not the superposition of pure metal Zr and X . To characterize the impact of Zr- X bond on mechanical properties of alloys, the relative variation of mechanical parameters Q_M is introduced for alloy systems,

$$Q_M = \frac{2M^{Zr-X} - (M^{Zr-Zr} + M^{X-X})}{(M^{Zr-Zr} + M^{X-X})} 100\% \quad (9)$$

where M^{Zr-X} are mechanical properties of Zr- X bond estimated from *hcp* unit cell with one Zr atom and one X atom, M^{X-X} are mechanical properties of X - X bond estimated from X_2 *hcp* unit cell. Either a positive or negative of Q_M indicates an enhanced or suppressed effect of Zr- X bond to the mechanical properties of Zr X alloys, and the numerical magnitude indicates the strength of this effect. Q_M ($M=C_{11}, C_{33}, C_{12}, C_{13}, C_{44}, B, G, \nu$ and B/G) for Zr- X alloy systems are listed in Table IV, where Q_B of Zr-Ti system (-6.31) implies that Zr-Ti bond has a suppressed effect on the bulk modulus of Zr-Ti system, Q_B of Zr-Hf system (0.74) and Zr-Sc systems (0.38) show that the effect of Zr- X bond on bulk modulus of Zr-Hf and Zr-Hf systems is negligible. Hence bulk modulus B has parabolic composition dependence in Zr-Ti system but exhibit linear composition dependence in Zr-Hf and Zr-Sc systems, which can be observed from Fig. 2 and Fig. 3. For

Table 4: The relative variation of mechanical parameters Q_M for Zr- X alloy systems, where M are C_{11} , C_{33} , C_{12} , C_{13} , C_{44} , B , G , ν and B/G .

	$Q_{C_{11}}$	$Q_{C_{33}}$	$Q_{C_{12}}$	$Q_{C_{13}}$	$Q_{C_{44}}$	Q_B	Q_G	Q_ν	$Q_{B/G}$
Zr-Ti system	-20.41	-9.95	15.32	-1.04	-21.45	-6.31	-36.02	13.28	44.36
Zr-Hf system	0.21	5.05	6.34	-4.51	3.51	0.74	2.60	-2.02	-7.37
Zr-Sc system	10.49	-0.96	-16.19	-3.03	27.61	0.38	24.47	-8.15	-19.90

Zr-Ti system, the maximum and minimum of Q_M are $Q_{B/G}$ (44.36) and $Q_{C_{13}}$ (-1.04) implying that they should have the biggest and smallest curvature, respectively, which also can be observed from Fig. 2.

Bulk modulus (Fig. 2(g), Fig. 3(c), Fig. 3(d)) as a function of alloy concentration can be perfectly described by the function (8). This phenomenon is caused by SQS templates. In fact the function (8) is supposed to describe all mechanical properties of random alloys well. However in the present work, alloys are described by SQSs that would lower the symmetry of systems and bring about fitting deviations. To confirm this idea, mechanical properties of six structures with the same composition 0.5 but different atomic arrangements for Zr-Ti were calculated where structure 1 is *hcp* unit cell, 2-5 are SQSs-8 possessing different correlation function, 6 is SQS-16. The results (Fig. 4) indicate that bulk modulus has little to do with atomic configuration while other mechanical properties are more sensitive to atomic configuration. That is why bulk modulus as a function of alloy concentration can be better described by the function (8) than other mechanical properties. In fact, this is because bulk modulus is an average effect of atomic configuration instead of depending on a single lattice direction.

Figure 4: (Color online) Mechanical properties of six structures with the same composition but different in atomic arrangement for Zr-Ti where structure 1 is *hcp* unit cell, 2-5 are SQS-8, 6 is SQS-16 based on *hcp* unit cell.

Besides the Euclidean distance deviations P is employed to characterize the degree of elastic symmetry deviations, where the higher value of P is, the more deviations the structure has. For pure metal Zr, Ti, Hf and Sc, one should find *hcp* symmetry exactly, *i.e.*, $P = 0$. However in our calculations, we find $P =$

1.05% for Zr, $P = 0.084\%$ for Ti, $P = 0.20\%$ for Hf and $P = 0.18\%$ for Sc. This kind of deviation introduced by the first-principles method gives an estimate to numerical errors in calculating elastic constants. The highest one (1.05%) among them is regarded as global numerical errors. In Fig. 5, the P for concentration 0.25, 0.5 and 0.75 are considerably higher than global numerical error (the blue line) but smaller than 8.0%, which implies that the symmetry deviations bring by supercell size cutoff errors are not negligible but acceptable[11]. For Hf-Zr system, P are smaller than global numerical error, which means that the symmetry deviations introduced by supercell size cutoff errors are negligible. In Fig. 5, the value of P for Sc-Zr alloy is smaller than global numerical errors except at concentrations 0.5 and 0.75, which means in most regions of concentration symmetry deviations are negligible. Deviations at concentrations 0.25 and 0.75 are great than deviation at concentration 0.5 in Zr-Ti and Zr-Hf systems. One possible reason is that the correlation functions and symmetry of SQSs at 0.25 and 0.75 are lower than that of SQSs at 0.5. However this explanation is not confirmed because the trend is opposite in Zr-Sc system. But we notice that it consumes more time to calculate the mechanical properties at Ti concentration 0.25 (0.75) than at Ti concentration 0.5.

Figure 5: (Color online) Euclidean distance deviations $P = \|C - C^{hcp}\|/\|C\|$ for Zr-X alloy systems. The black line indicates global errors of first-principles methods in calculating elastic tensor.

4. Conclusions

In this study, using the first-principles approach in conjunction with the special quasi-random structures (SQSs), the mechanical properties of Zr- X ($X = \text{Ti, Hf and Sc}$) alloy systems have been systematically investigated. The dependence of the mechanical coefficient such as elastic constants and elastic modulus on alloy composition has been examined. We have found that the ductility of Zr can be enhanced by alloying with Ti, whereas it would get worse if alloying with Hf or Sc. For these alloy systems, mechanical parameters change smoothly with alloying concentration, and can be well described by the function (8). We hope the theoretical findings presented and discussed in this work can help us to gain an in-depth understanding of the alloying effect on the mechanical properties of alloys.

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Author Contributions

Sunchao Huang, Yongsheng Zhang, Xiaoli Zhang, Zongguo Wang, Xiaoyu Yang and Zhi Zeng conceived the research as well as reviewed the manuscript. Sunchao Huang carried out the calculations and wrote the main manuscript.

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Special quasi-random structure (SQS)