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First-principles calculation of structural and elastic properties of $Pd_{3-x}Rh_xV$ alloys

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Abstract: The structural stability, electronic and elastic properties of $Pd_{3-x}Rh_xV$ alloys with $L1_2$ and $D0_{22}$ structures were investigated theoretically by the first-principles calculations. The results reveal that with the increase of Rh content, the unit cell volume of $Pd_{3-x}Rh_xV$ alloys with $L1_2$ and $D0_{22}$ structures decreases, and the structure of $Pd_{3-x}Rh_xV$ alloys tends to transform from $D0_{22}$ to $L1_2$. The elastic parameters such as elastic constants, bulk modulus, shear modulus, elastic modulus, and Poisson ratio, were calculated and discussed in details. Electronic structures were also computed to reveal the underlying mechanism for the stability and elastic properties.

Key words: $Pd_{3-x}Rh_xV$ alloys; first-principle calculations; electronic structure; elastic properties

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1 Introduction

The transition metals and their inter-metallic alloys are promising structural materials because of their high melting points, high strength, and good oxidation resistances[1]. In recent years, the inter-metallic alloys have attracted considerable experimental and theoretical interests of many researchers[2]. Experimental results on many inter-metallic alloys reveal that the $L1_2$ atomic order is significantly more ductile than the $D0_{22}$ order, due to the lack of a sufficient number of slip systems in the $D0_{22}$ structure[3]. Consequently, the $L1_2$ alloys are more suitable in structural applications because of their excellent mechanical properties[4]. Whereas the $D0_{22}$ structure is an ordered tetragonal phase and closely related to the $L1_2$ structure (by a 1/2 [110] shift on every (001) plane). Through part replacement of high e/atom atoms in $D0_{22}$-based alloys with low e/atom atoms, the $D0_{22}$-based alloys can be transformed into the $L1_2$ structure[5]. Therefore, it is expected that the mechanical properties of these modified $D0_{22}$-based alloys can be improved because of the availability of more slip systems in the $L1_2$ structure[6].

Recent studies proved that it is possible to modify the microstructure of $D0_{22}$. For example, LIU[7] found that although Ni_3V compound is prone to crystallize into the tetragonal $D0_{22}$ structure. by adding Co and Fe into Ni_3V, the pseudobinary compound $(Ni, Co, Fe)_3V$ can be stabilized either in the cubic $L1_2$ structure or in the tetragonal $D0_{22}$ structure, depending on the Co or Fe content. The reason is that Co or Fe has lower e/atom than Ni, so the addition of Co or Fe to Ni_3V can lower the overall e/atom to an appropriate value. In addition, similar experimental study was performed for Pd_3V and Rh_3V compounds[8]. It was found that the Pd_3V alloys are prone to crystallize into the tetragonal $D0_{22}$ structure, while the Rh_3V alloys prefer to $L1_2$ structure[8−9]. Hence, it is expected that substituting Pd by Rh can stabilize the $L1_2$ structure and further improve the mechanical properties of Pd_3V-based compounds.

Nowadays, *ab initio* calculations are extensively

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used to predict the structure, stability and mechanical properties of pseudobinary alloys[10]. In order to get a better understanding of structural stability and mechanical properties of $Pd_{3-x}Rh_xV$ alloys after the substitution of Pd with Rh in Pd_3V alloys, *ab initio* theoretical calculations of $Pd_{3-x}Rh_xV$ inter-metallic compounds are necessary. The main aim of this study is to investigate the effect of substitution of Pd with Rh on the structural stability and mechanical properties, and provide valuable theoretical results to optimize and design the transition metal alloys.

2 Method of calculation

All calculations were done by using the Vienna *ab-initio* Simulation Package (VASP) program[11], which is based on density functional theory (DFT). The Perdew–Wang (PW91) version of the generalized gradient approximation (GGA)[12] was used to describe the exchange correlation function, and the projector augmented wave (PAW) method[13] was used in the present work. The cutoff energy (E_{cut}) of atomic wave functions was set at 350 eV. The Brillouin zone integrations used Monkhorst–Pack grids [14] of 12×12×12 for $L1_2$ and 12×12×8 for $D0_{22}$, respectively. The *k*-point was increased to 18×18×18 ($L1_2$) and 18×18×12 ($D0_{22}$) for the density of states (DOS) calculation. Atomic geometry optimization was performed by full relaxation with the conjugate gradient method until the total energy changes within 10^{-5} eV/atom and the Hellmann-Feynman force on all atomic sites was than 10^{-2} eV/Å. The first-order Methfessel-Paxton[15] method with a width of 0.2 eV was used for total energy calculations, and the calculations of density of states (DOS) were performed with the linear tetrahedron method with Bloch correction[16−17]. The elastic constants were obtained by calculating the total energy as a function of appropriate lattice deformation[18].

3 Results and discussion

3.1 Structural parameters

The structural optimization was firstly performed with the conjugate-gradient algorithm by full relaxation of unit cell volume and shape as well as the internal atomic positions. The equilibrium lattice constants were obtained from the minimum total energy. The lattice parameters for pure Pd, Rh, V and $Pd_{3-x}Rh_xV$ are reported in Table 1, together with the experimental and other theoretical results in Refs.[19−23]. For pure metal Pd, Rh, V, and alloys Pd_3V ($D0_{22}$) and Rh_3V ($L1_2$), the calculated values of lattice constants are in good agreement with the experimental values, implying that the calculation parameters chosen in this work are valid. In addition, it is noticeable that as the Rh content increases, the unit cell volume of $Pd_{3-x}Rh_xV$ decreases in both the $L1_2$ and $D0_{22}$ structures. Therefore, it can be concluded that the substitution of Pd with Rh leads to the contraction of $Pd_{3-x}Rh_xV$ alloy in both $L1_2$ and $D0_{22}$ structures.

Table 1 Calculated lattice constants, equilibrium volume *V* together with available experimental data

System	Calculated data			Experimental data
	a/Å	*c*/Å	*V*/Å^3	*a*/Å
Pure-Pd(fcc)	3.948			3.889[19]
Pure-Rh(fcc)	3.840			3.802[20]
Pure-V(bcc)	2.977			3.038[21]
$Pd_3V(L1_2)$	3.889	3.889	58.818	
$Pd_3V(D0_{22})$	3.872	7.817	117.195	3.847[22]
$Pd_2RhV(L1_2)$	3.813	3.953	57.473	
$Pd_2RhV(D0_{22})$	3.891	7.633	115.563	
$PdRh_2V(L1_2)$	3.870	3.750	56.163	
$PdRh_2V(D0_{22})$	3.828	7.724	113.184	
$Rh_3V(L1_2)$	3.805	3.805	55.089	3.784[23]
$Rh_3V(D0_{22})$	3.822	7.576	110.668	

3.2 Formation heat and cohesive energy

For the better understanding of the stability of $Pd_{3-x}Rh_xV$ alloys, the calculation of formation heat and cohesive energy was performed[24]. The average formation heat of $Pd_{3-x}Rh_xV$ alloy is defined as[25]:

$$\Delta\overline{H}=\frac{1}{x+y+z}(E_{tot}-xE_{solid}^{pd}-yE_{solid}^{Rh}-zE_{solid}^{V}) \quad (1)$$

where $\Delta\overline{H}$ is the average formation heat per atom; E_{tot} is the total energy of the unit cell; E_{solid}^{Pd}, E_{solid}^{Rh} and E_{solid}^{V} are the energy per atom of bulk Pd, Rh and V, respectively; *x*, *y* and *z* refer to the numbers of Pd, Rh and V atoms in unit cell.

The obtained formation heat of $Pd_{3-x}Rh_xV$ is shown in Fig.1. From Fig.1, it is found that for $L1_2$ structure, the negative formation heat of $Pd_{3-x}Rh_xV$ becomes lower when *x* increases from 0 to 3, so the $Pd_{3-x}Rh_xV$ alloys become more stable from the energetic point of view. While for the $D0_{22}$ structure, with the increase of *x*, the formation heat of $Pd_{3-x}Rh_xV$ is also smaller, indicating that the addition of Rh component in binary alloys (Pd_3V) also increases the stability of $D0_{22}$ crystal structure. In addition, it should be noted that when *x* is equal to 0 or 1，the heat formation of $D0_{22}$ structure is more negative than that of $L1_2$ structure, so the Pd_3V and Pd_2RhV are prone to $D0_{22}$ structure. When *x* is 2 or 3, the heat