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Theoretical investigation of hydrogen absorption properties of rhodium–silver alloys

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ABSTRACT

The density of states and the H absorption energy of Ag_xRh_{1-x} alloys were theoretically investigated by the first-principles method. The electronic structure of the alloys near the Fermi edge was similar to that of Pd, which is known as hydrogen-storage metal, and this indicated the electronic state at the part plays important role to determine the H absorption property. The results showed that the H absorption into the Ag_xRh_{1-x} alloys was thermodynamically stable and the trend of composition dependence agreed well with the experimental observation. Considering the atomic configuration of alloys, homogeneous structure is found to be a key in the emergence of H absorption nature in this alloy system.

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1. Introduction

The transition metals such as Pd, Pt and other elements are known as good catalysts or the H absorption metals. It is generally known that alloying in the atomic level brings the functionality different from that of mono-element materials [1–11]. Recently, Kusada et al. [12] successfully fabricated through a novel synthesis method the homogeneously mixed alloy nanoparticle of Rh and Ag, which is well known as the thermodynamically immiscible combination in the bulk [13]. It was found that the Ag–Rh alloy systems absorb the hydrogen like Pd locating between Rh and Ag in the periodic table, while bulk Rh or Ag do not absorb hydrogen. The composition dependence of the amount of the absorbed H is also observed: $Ag_{0.5}Rh_{0.5} > Ag_{0.4}Rh_{0.6} > Ag_{0.7}Rh_{0.3}$. The work proved that we can arbitrarily reproduce or control the material property with the alloys of which combination of the elements and the compositions are infinity. The correlation between the H absorption property and the electronic structure is well discussed the former literature by Klein and Papaconstantopoulos et al. [14–16] To understand the origin of Pd like property observed in Ag–Rh alloy systems, Seo et al. theoretically studied the H absorption and electronic structure of the $Ag_{0.5}Rh_{0.5}$ alloy using a super cell (layered) structure [17]. We also have studied the electronic structure of $Ag_{0.5}Rh_{0.5}$ alloy both experimentally and theoretically to find the similarity between Ag–Rh alloys and Pd in the electronic states near the Fermi level [18]. As a next step to understand the unique properties of $Ag_{0.5}Rh_{0.5}$ alloy, we theoretically investigated the hydrogen absorption properties in this study. Hydrogen absorption occurs through gas phase diffusion, adsorption, and dissociation of hydrogen molecules followed by migration of atomic hydrogen into the interstitial sites of metals. Among those processes, we focus on the state of absorbed hydrogen in the metal, which is observed in the preceding experimental study [12]. In this manuscript, to discuss the detail influence of alloy compositions and configurations on the electronic structures and H absorption properties of Ag_xRh_{1-x} ($0 \leq x \leq 1$) alloys, the computational work based on the density functional theory (DFT) calculations with various configuration models is presented.

2. Computational method and calculation details

We employ the alloy models made from the rhombohedral cells consisting of the eight metal atoms of Rh and Ag, i.e. Ag_xRh_{1-x} alloys

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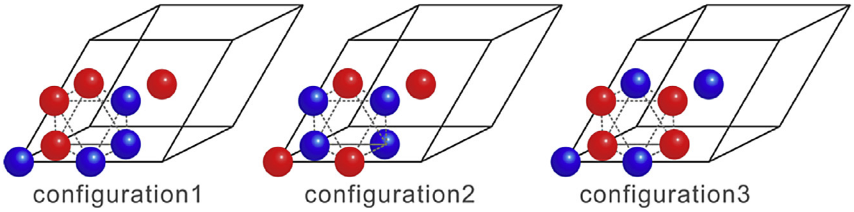

Fig. 1. Calculation models. Red and blue spheres show the Ag and Rh atoms. The figure shows the examples of $Ag_{0.5}Rh_{0.5}$ alloy that have three non-equivalent configurations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(x = 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, 1). A small sized model is chosen to avoid the complexity of many possible configurations in larger model and to concentrate on the discussion of the local configuration. Fig. 1 shows the three non-equivalent configurations for the $Ag_{0.5}Rh_{0.5}$ alloy. The non-equivalent configurations contain a different set of octahedral sites. For example, there are three configurations for $Rh_{0.5}Ag_{0.5}$ alloy model as shown in Fig. 1. For configuration 1, there are eight octahedral sites that consist of 3Rh and 3Ag atoms (Ag_3Rh_3 site). For configuration 2, there are three types of octahedral site: Two sites consist of 4Rh and 2Ag atoms (Ag_2Rh_4), four are Ag_3Rh_3 and the remaining two are Ag_4Rh_2. Configuration 3 has four Ag_2Rh_4 and four Ag_4Rh_2 sites. To classify the configurations, we analyzed the homogeneity of the alloys. As an index for homogeneity of the alloys, we used the standard deviation of the composition, i.e. the variation of the local composition of the octahedral sites from the overall alloy composition. Thus, the standard deviation σ is obtained by following equation:

$$\sigma = \sqrt{\sum_{\text{site}} (c - x)^2 \cdot n_{\text{site}}}. \tag{1}$$

c and x are the compositions of Rh for the site and the whole alloy, respectively. n_{site} is the number of the sites. The components and the numbers of the sites for each alloy and the standard deviation are shown in Table 1. For the configuration 1 of $Ag_{0.75}Rh_{0.25}$, there are four Ag_5Rh_1 sites ($n_{\text{site}} = 4$ and $c = 1/6$) and four Ag_4Rh_2 sites ($n_{\text{site}} = 4$ and $c =$ ca. 1/3). As a result, the standard deviation is obtained as 0.083. The configurations are numbered in the order of decreasing homogeneity.

We calculated the H absorption energy for $Ag_xRh_{1\text{-}x}H_y$ ($y = 0.125, 1.0$) i.e. the models that contain one or eight H atoms in interstitial octahedral sites. The H absorption energy (ΔE_H) is calculated by the following equation:

$$\Delta E_H = \{E_{M-H} - (E_M + n/2 \cdot E_{H2})\}/n. \tag{2}$$

In this work, zero-point energy is not considered. For all the total energy calculations, we used the DFT program with the projector augmented wave method, as implemented in the Vienna Ab initio Simulation Package (VASP) [19–22]. The Perdew-Burke-Emzerhof [23] functional with a generalized gradient approximation is used for the exchange and correlation interactions. For the plane-wave basis sets, cut-off energies of 400 and 700 eV are used for geometry optimization and density of states (DOS) calculations, respectively. The convergence threshold for self-consistent field calculations is 1.0×10^{-5} eV/atom. After carefully checking the energy convergence with the parameter such as cut-off energy or the number of k-points, we found that the energy fluctuation is less than ~10^{-3} eV when the k-points sampling of 10 × 10 × 10. We thus selected 14 × 14 × 14 k-points sampled by the Monkhorst-Pack gridding method [24]. The cell and atomic positions are optimized in advance by a conjugate gradient method with tolerances of 1.0×10^{-4} eV/atom.

Table 1
Configurations and homogeneity.

configurations	Sites	Number of the sites and homogeneity								
		Rh	$Ag_{0.125}Rh_{0.875}$	$Ag_{0.25}Rh_{0.75}$	$Ag_{0.375}Rh_{0.625}$	$Ag_{0.5}Rh_{0.5}$	$Ag_{0.625}Rh_{0.375}$	$Ag_{0.75}Rh_{0.25}$	$Ag_{0.875}Rh_{0.125}$	Ag
1	Rh_6	8	2							
	Ag_1Rh_5		6	4						
	Ag_2Rh_4			4	6					
	Ag_3Rh_3				2	8	2			
	Ag_4Rh_2						6	4		
	Ag_5Rh_1							4	6	
	Ag_6								2	8
	Standard deviation	0.000	0.072	0.083	0.072	0.000	0.072	0.083	0.072	0.000
2	Rh_6			2						
	Ag_1Rh_5				2					
	Ag_2Rh_4			6	2	2				
	Ag_3Rh_3				4	4	4			
	Ag_4Rh_2					2	2	2		
	Ag_5Rh_1						2			
	Ag_6							6		
	Standard deviation			0.144	0.138	0.118	0.138	0.144		
3	Rh_6									
	Ag_1Rh_5									
	Ag_2Rh_4					4				
	Ag_3Rh_3									
	Ag_4Rh_2					4				
	Ag_5Rh_1									
	Ag_6									
	Standard deviation					0.167				

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