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Analysis of the electronic structure of zirconium hydride

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Abstract

The electronic structure of zirconium hydride was analyzed by a discrete-variational (DV)-Xα molecular orbital method. The density of states of zirconium hydride estimated by DV-Xα calculation agreed with X-ray photoemission spectroscopy spectra of zirconium hydride. The net charges of Zr atom and H atom were found to be small and independent of the hydrogen content. While the Zr–Zr bond order decreased with the hydrogen content, the Zr–H bond order was hardly affected by the hydrogen content. The mechanical properties such as elastic modulus were qualitatively discussed on the basis of the results for the molecular orbital calculation.

Keywords: Zirconium hydride; DV-Xα method; Electronic structure; Bond order; Elastic modulus

1. Introduction

Zirconium alloys such Zircaloy and Zr–Nb have been widely used as the nuclear materials of fission reactors such as light water reactors (LWRs) and Canadian deuterium uranium reactors (CANDUs). Since hydrogen behavior in the cladding and in the pressure tube is closely associated with the hydrogen embrittlement, therefore, it is necessary to understand the physicochemical properties of zirconium hydride such as mechanical and thermal properties. In the previous study, the physicochemical properties such as mechanical and thermal properties of zirconium hydride and deuteride have been examined [1,2]. In the present study, the electronic structure of zirconium hydride has been analyzed by a discrete-variational (DV)-Xα molecular orbital method, and the physicochemical properties of the zirconium hydride were discussed on the basis of the results of the calculation.

2. Computational procedures

Molecular orbital calculation was performed by means of a DV-Xα cluster method based on the local density function approximation. The DV-Xα method is a non-relativistic first-principles method using Slater's Xα potential as the exchange-correlation potential. The details of the DV-Xα method have been described in the literature [3–5]. The Slater's exchange parameter, α was fixed at 0.7 for all the atoms. The basis sets of numerical atomic orbitals used were 1s–5p, and 1s for Zr, H, respectively. In order to evaluate the overlap population, the Mulliken population analysis was employed [6,7]. Four clusters were used for the hcp metal and CaF_2 type δ-hydrides with hydrogen contents of 1.00, 1.50, and 2.00 H/Zr. The cluster model of $\delta ZrH_{2.00}$ is shown in Fig. 1. In all the hydride clusters, H atoms were arranged symmetrically around the center. The lattice parameters obtained in our previous study [2] were used for the calculation.

3. Experimental

The electronic states of zirconium metal and hydride were examined by X-ray photoemission spectroscopy (XPS). The measurement was carried out by a QUANTUM 2000 spectrometer supplied by Physical Electronics. All the zirconium hydride samples showed CaF_2 type δZrH_{2-x}, and the hydrogen contents of the samples were 1.52, 1.65, and 1.74 H/Zr. The XPS spectra were measured using an Al K_α (1486.6 eV) X-ray source with a fixed analyzer resolution of 0.25 eV and the analysis area

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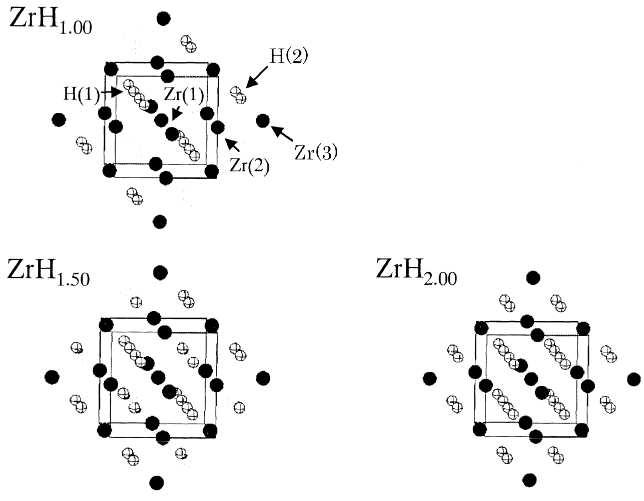

Fig. 1. Cluster model used in the calculation for zirconium hydride. The larger and smaller spheres represent Zr and H atoms, respectively. Different numerical labels enclosed in parentheses denote inequivalent atoms in the cluster.

was 300 nm×300 nm. The surface of samples was sputtered with Ar ion for 15 min in a vacuum below 10^{-6} Pa.

4. Results and discussion

Fig. 2 shows the density of states (DOS) obtained by the DV-Xα calculation and the XPS spectra. The results obtained in the present study agreed with the literature data [8,9]. In the DOS diagrams of the zirconium metal and hydride in the calculation shown in Fig. 2b and c, the Zr 4d peak appears at about 1 eV below Fermi energy E_F. The Zr 4d peak of zirconium hydride is smaller than that of the metal. In the DOS diagram of zirconium hydride shown in Fig. 2b, the peak is generated in the vicinity of 6.5 eV below E_F. This peak becomes larger with increasing hydrogen content. From Fig. 2c and d, it is obvious that this peak resulted from interaction between Zr 4d and H 1s electrons. In order to elucidate the interaction, the overlap populations of both Zr–Zr and Zr–H bonds was examined, as shown in Fig. 3. This figure indicates that this interaction was the Zr 4d–H 1s bonding-type interaction. As the hydrogen content in the hydride increases, the magnitude of Zr 4d and Zr 4d interaction becomes weaker and that of Zr 4d and H 1s interaction hardly changes. The density of states of zirconium hydride estimated by DV-Xα calculation agreed with the XPS spectra of zirconium hydrides. Therefore, a qualitative discussion about physicochemical properties of zirconium metal and hydride appears to be possible on the basis of the results for the DV-Xα calculation.

In the previous study [1], the mechanical properties of zirconium metal and hydride have been examined. Fig. 4 shows the changes in Young's modulus and compressibility of zirconium hydride with the hydrogen content. We attempted to discuss about elastic properties with the bond order and the net charge in DV-Xα calculation. Fig. 5 shows the change in the net charge in Zr atom and H atom

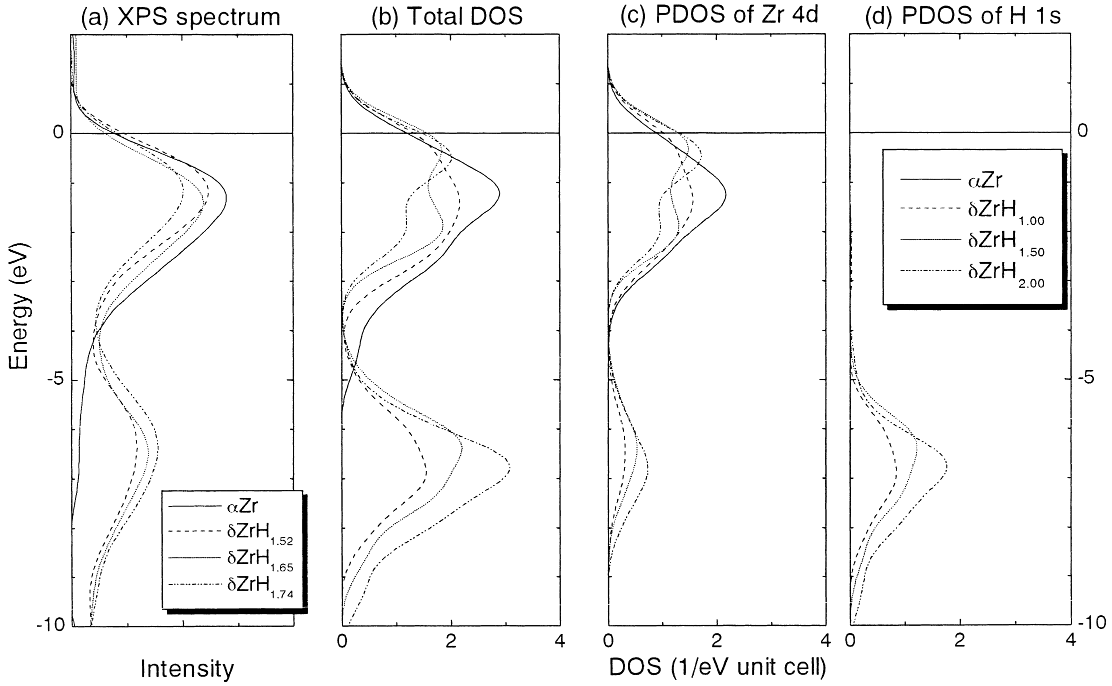

Fig. 2. XPS spectrum and total and partial density of states for zirconium metal and hydride. (a) XPS spectrum, (b) total density of states, (c) partial density of states of Zr 4d, (d) partial density of states of H 1s.

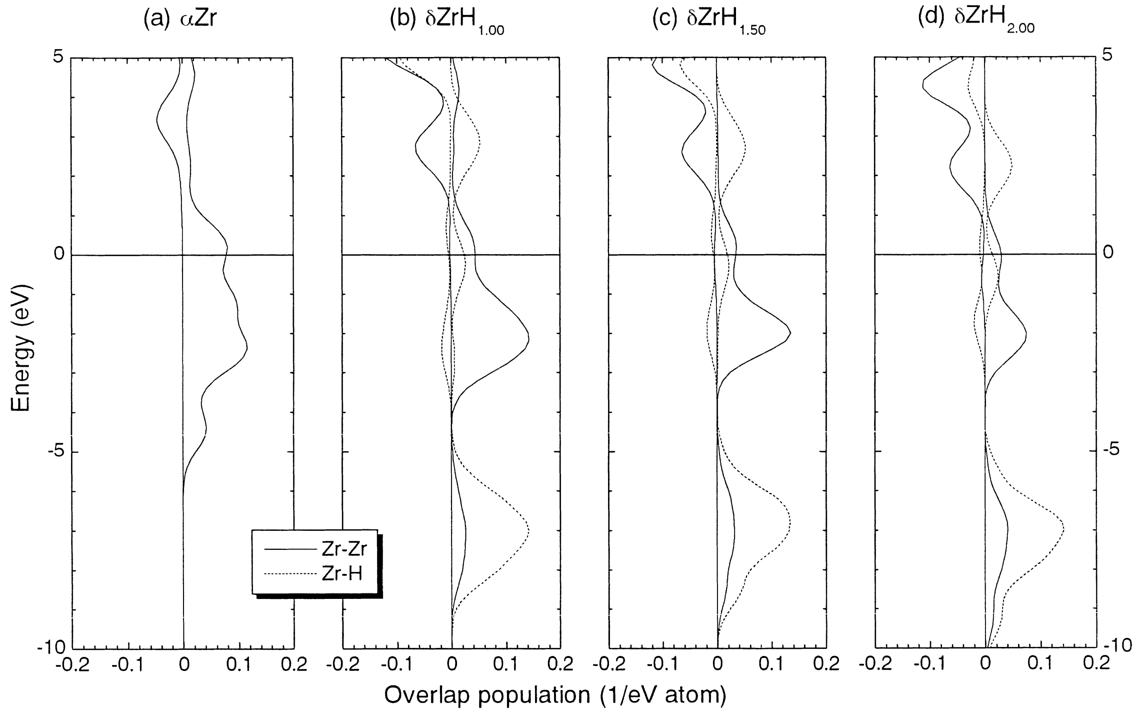

Fig. 3. The overlap population diagram for zirconium metal and hydride (a) αZr, (b) $\delta ZrH_{1.00}$, (c) $\delta ZrH_{1.50}$, (d) $\delta ZrH_{2.00}$.

with the hydrogen content. The net charge is a measure of the strength of the ionic bond. The net charge in Zr atom and H atom is small and independent of the hydride content. Therefore, the covalent bond is mainly dominant in the bond of zirconium hydride. Fig. 5 shows the change in the Zr–Zr and Zr–H bond order with the hydrogen content. The bond order shown in this figure is the value per atomic bond in the cluster and a measure of the strength of the covalent bond between atoms. The Zr–Zr bond order decreases with the hydrogen content, whereas

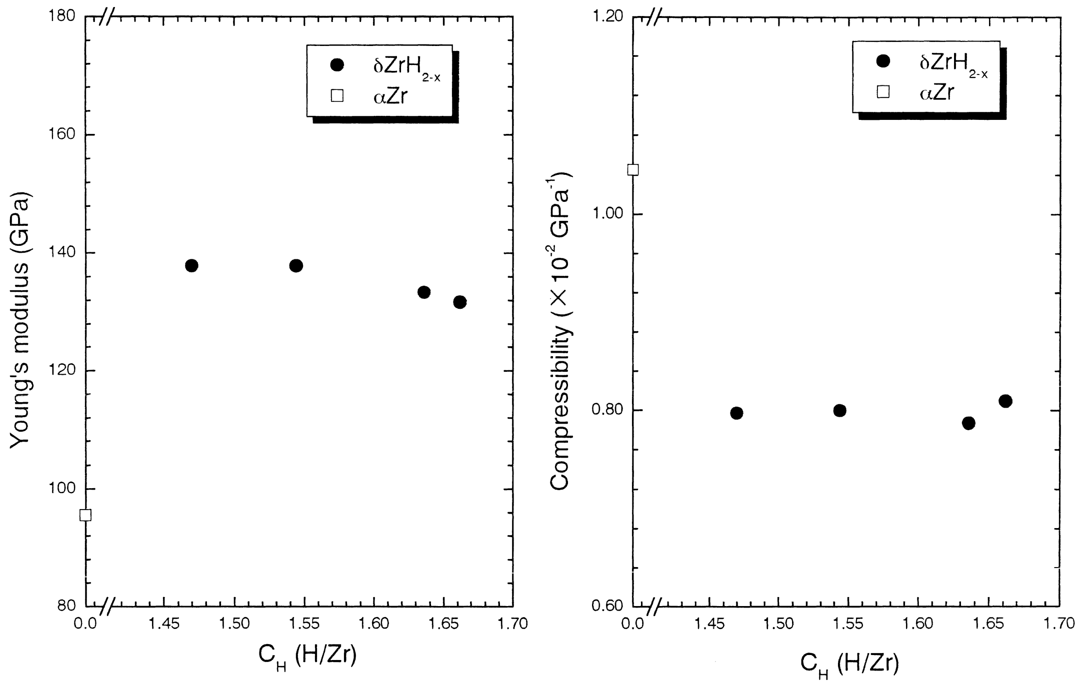

Fig. 4. The changes in Young's modulus and compressibility of zirconium hydride with the hydrogen content.

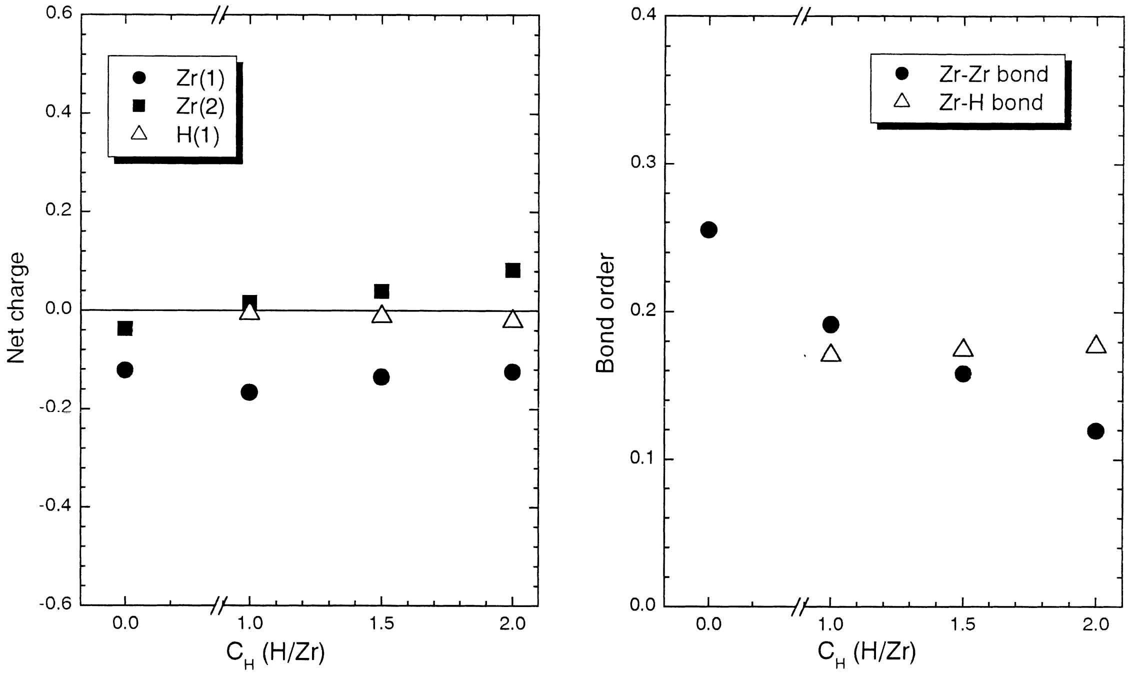

Fig. 5. The change in the net charge and the bond order of zirconium hydride with the hydrogen content.

the Zr–H bond order is hardly affected by the hydrogen content.

The depth of interatomic potential is closely related to the bond strength. Therefore, as the bond order is large, the depth of interatomic potential is generally large. The elastic moduli depend on the slope in the vicinity of the bottom of the interatomic potential that can be expressed approximately as a quadratic form. As the depth of interatomic potential is large, elastic moduli appear to be large. Consequently, the elastic moduli increase with increasing bond order.

The elastic moduli of zirconium metal and hydride are discussed in terms of the spring model. In this model, the spring constant corresponds to the elastic modulus. The entire spring constant of zirconium hydride appears to be larger than that of the metal since the Zr–Zr bond in the hydride is reinforced with the Zr–H bond. Larger elastic modulus is observed for the hydride than for the metal.

The elastic moduli of the zirconium hydride slightly decreased with the hydrogen content. In the hydride, the spring constant for Zr–Zr bond decreases with the hydrogen content, and the Zr–H bond hardly changes with the hydrogen content. This suggests that the entire spring constant of zirconium hydride decreases with the hydrogen content. The change in the elastic properties of the zirconium hydride appears to be qualitatively explained by the results of DV-Xα molecular orbital calculation. The micro hardness of the zirconium hydride appears to be interpreted with the same model as the elastic properties based on the DV-Xα calculations. The results for the DV-Xα calculation will be applied to the thermal properties of the zirconium hydride such as the thermal expansion coefficient.

5. Conclusions

The electronic structure of zirconium hydride was estimated by DV-Xα molecular orbital calculation. In the DOS diagram of zirconium hydride, the peak was generated in the vicinity of 6.5 eV below E_F, and this peak appeared to result from the bonding-type interaction operating between Zr 4d and H 1s electrons. The density of states of zirconium hydride in this calculation agreed with the XPS spectra of zirconium hydrides. The net charge in Zr atom and H atom was found to be small and independent of the hydrogen content. While the Zr–Zr bond order decreased with the hydrogen content, the Zr–H bond order was hardly affected by the hydrogen content. The influence of the hydrogen content on the elastic moduli of zirconium hydride were qualitatively explained with the Zr–Zr and Zr–H bond order obtained by the DV-Xα calculation.

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