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Calculation of electronic structure at bonding interface between vanadium and oxide ceramics for insulator coating applications

M. Satou *, N. Komatsu, T. Sawada, K. Abe

Department of Quantum Science and Energy Engineering, Tohoku University, 01 Aramaki-aza-Aoba, Aoba-ku, Sendai 980-8579, Japan

Abstract

Fundamental understanding of metal and ceramics bonding will provide useful guideline to develop a robust coating material for fusion reactor application. We have studied the bonding interface using the model that had three layers of CaO slab adhered to both sides of three layers of V slabs by means of the electronic structure calculation. The simple interface model of vanadium and CaO facing each other at the (0 0 1) plane was employed. Total energy and adhesive energy were evaluated. We found that the relation of adhesive energy and separation distance of the interface is described well by the Rydberg function. The ideal strength of the interface was calculated to be 6.4 GPa. It is proposed that these methods could be applied to systematic development of robust coating materials for fusion applications.

1. Introduction

Development of electrical insulator coatings is identified as a key issue to reduce magnetohydrodynamic (MHD) pressure drop in liquid metal cooling blanket design for a high-magnetic-field fusion reactor. Metal and ceramic bonds are typical structures of blanket designs. In previous studies of metal and ceramics bonding, a solid-state diffusion bonding experiment showed that vanadium alloys form direct bonding with oxide ceramics without intermediate reaction layer, while the bonding with nitride ceramics form intermediate reaction layers [1,2]. Because of the intrinsic difficulty in obtaining experimental parameters of the interface, understanding of the bonding by means of atomistic scale modeling will provide useful guidelines to develop a robust coating material. Since a couple of decades, ab initio simulation methods have made remarkable progress with computational capabilities. Several well-packaged calculation codes for solid-state physics application are available [3]. Previous fundamental studies were carried out on simple interfaces that is strain-free, strong adhesive bonds, nearly the same coefficients of thermal expansion, without intermediate phase, well-characterized interfacial atomic structure, such as MgO/V [4] and Al_2O_3/Nb [5], etc. We attempt to apply these calculation methods to the selected primary candidates materials for the MHD insulator coating, such as CaO, Er_2O_3 and Y_2O_3 on vanadium alloy.

2. Methods

2.1. Calculation models

A combination of CaO and V was selected in this study. CaO has sufficient electrical resistivity (10^7 Ω m at 1023 K [6]), adequate compatibility with lithium up to 873 K [7] and possible self-healing capability [8]. Although the other candidate ceramics for the insulators include Y_2O_3 and Er_2O_3 have much better compatibility with lithium at high-temperatures [9], CaO was selected here due to its rather simple structure. CaO has rock-salt structure with face centered cubic lattice. The

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[*] Corresponding author. Tel./fax: +81-22 217 7924.
E-mail address: manabu.satou@qse.tohoku.ac.jp (M. Satou).

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experimental lattice parameter used in the calculation for CaO was 0.481059 nm, and that for V was 0.30274 nm with body centered cubic lattice. Previous electronic structure calculations indicated that early transition metals (V, Nb, Ti) and oxide ceramics have strong bonding. The metal atoms were located directly on the top of the oxide O ions [10]. Experimental observation of the interface between V and MgO, that has rock-salt structure, showed that the interface was coherent [4]. In this paper, a simple interface model of CaO and V facing each other at the (0 0 1) plane was employed for the calculation. When the orientation of the interface was chosen to be the same as the MgO and V interface [4], that is, the V lattice is rotated by π/4 around the [0 0 1] axis of the CaO lattice, a lattice misfit as large as 11% was calculated. The model we used here is that the V lattice is rotated by $(\pi/4 - \arctan(1/2))$ degree around the [0 0 1] axis of the CaO lattice, so that one out of five V atoms in the (0 0 1) plane are located on the top of O ions of the CaO as show in Fig. 1. We used a supercell approach to simulate the interface. Three layers of CaO slab is adhered to both sides of three layers of V slabs. These slabs repeat periodically as show in Fig. 2. The experimental lattice constant of 0.30274 nm was used for the V layers, so the CaO ($a = 0.481059$ nm) must shrink by 0.5% to be commensurate.

2.2. Calculation methods

For calculations of the electronic structure of the interface we have used the WIEN2k package [11]. Several well-packaged codes for the calculation of electronic structures are available with various choices of treatment of core electrons, functional and basis set, etc. WIEN2k uses density functional theory based on the full-potential linearized augmented plane-wave and local orbitals method. The exchange correlation energy of the electrons is described in the generalized gradient approximation using the Perdew–Burke–Ernzerhof functional [12]. Basis functions were expanded in combinations of spherical harmonic functions inside non-overlapping atomic spheres (muffin-tin sphere) and a plane wave expansion in the interstitial region. In the muffin-tin spheres, the l-expansion of the non-spherical potential and charge density was carried out up to $l_{\max} = 10$. We have expanded the basis function up to $R_{\mathrm{MT}}K_{\mathrm{MAX}} = 7$, where K_{MAX} is the maximum modulus for the reciprocal lattice vector and R_{MT} is the average radius of the muffin-tin spheres. The muffin-tin radius of 2.0, 2.0 and 1.6 atomic units were used for V, Ca and O atoms, respectively. A k-point sampling on a $6\times 6\times 3$ mesh generated according to the Monkhorst–Pack scheme [13] was used for the interface models. Total energy and adhesive energy of the interface were evaluated. A charge convergence limit of 0.0001 was applied to all calculation. The numerical accuracy of the energy was less than 0.1 meV/atom.

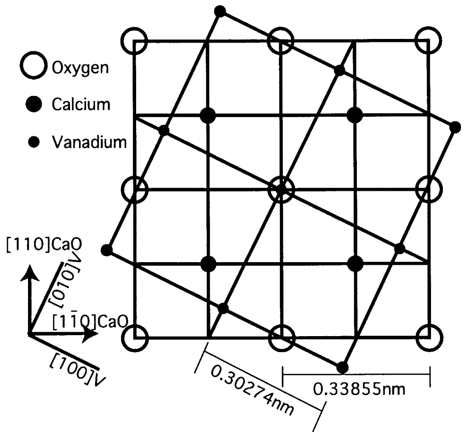

Fig. 1. Geometry of the CaO/V interface model. Vanadium and CaO are facing each other at the (0 0 1) plane in the interface.

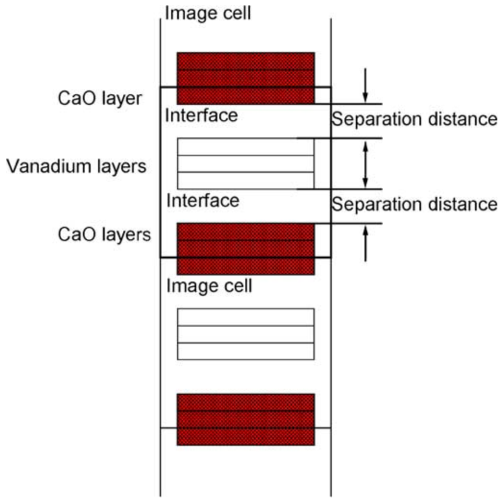

Fig. 2. Schematic representation of the geometric structure of the CaO/V interface model (side view). The dashed lines are corresponding to a supercell.

3. Results and discussion

3.1. Adhesive energy of the interface

Fig. 3 shows calculated total energy as a function of interface separation distance between CaO and V. The energy has the minimum at the distance of 0.32 nm, which is corresponding to the equilibrium separation. The adhesive energy (E_a) of the interface is defined as follows:

$$E_a = (E_{\mathrm{CaO/V}} - (E_{\mathrm{CaO}} + E_{\mathrm{V}}))/2A.$$

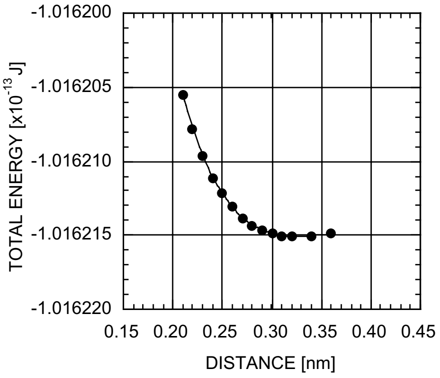

Fig. 3. Total energy as a function of separation distance of the CaO/V interface. The solid line is a visual guide.

$E_{CaO/V}$ is the total energy of the supercell containing the CaO and V interfaces, E_{CaO} and E_V refer to the energy of a slab of CaO or V, respectively, separated by vacuum. The area of an interface is A and the factor 2 represents the two interfaces in the supercell. Fig. 4 shows calculated adhesive energy as a function of the interface distance. The minimum energy at the equilibrium separation is defined as the ideal adhesive energy (E_0) of the interface.

The relation of adhesive energy and separation distance of covalent or metallic bond phases was described by the Rydberg function as follows [14]:

$$E^*(a^*) = -(1 + a^*)\exp(-a^*),$$

$$a^* = (d - d_0)/l.$$

$E^*(a^*)$ is a scaled adhesive energy, which is the adhesive energy (E_a) divided by the ideal adhesive energy (E_0), d is the separation distance, d_0 is the equilibrium separation distance and l is a scaling length. The scaling length l was chosen by hands here. As shown in Fig. 5, the function describes very well the relation of adhesive energy and separation distance for the CaO and V interface. This may indicate that covalent or metallic bonding between CaO and V contribute to the energy. More detailed analysis including charge density distribution is needed. For comparison, the plot of the simplest model with single layers of CaO and V is also shown in Figs. 4 and 5.

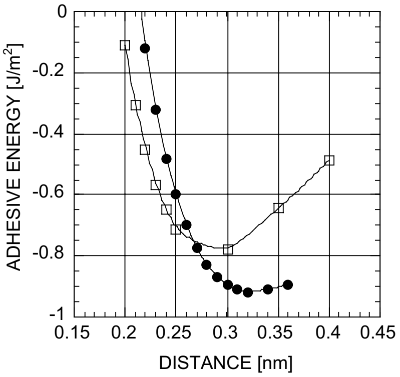

Fig. 4. Adhesive energy as a function of separation distance of the CaO/V interface. The solid circles represent three layers model, and the open squares represent single layers model. The solid lines are visual guides.

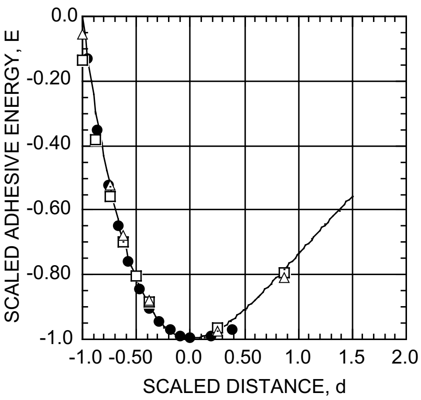

Fig. 5. Scaled adhesive energy as a function of scaled separation distance of the CaO/V interface. The solid circles represent three layers model, the open squares represent single CaO/V layers model. The open triangles represent single CaO/V–20Ti layers model. The solid line is a plot of the Rydberg function described in text.

3.2. Interfacial strength and effect of alloying elements

The stress can be defined as the derivative of the energy as a function of the separation distance. Hong [15] derived the ideal peak interfacial strength from the relation of the ideal adhesive energy as follows:

$$\sigma_{max} = 2E_0/le,$$

where $E_0 = 0.92$ J/m^2, $l = 0.105$ nm in the case of the CaO and V interface from Fig. 5 and e is the base of the natural logarithm. Thus the ideal strength of the interface is calculated to be 6.4 GPa. This value is several times lower compared to the interface used for modern high-temperature structural materials [15]. It is known that titanium addition improves the strength of the interface between V and oxide ceramics [1]. In Fig. 5,the results for the single layers model of the interface between V–20Ti alloy and CaO are also plotted. The ideal strength was the same as that of the single layers model of the interface between vanadium and CaO. Most of the practical interfaces may have segregation of solute atoms or impurities. For instance, a few atom layers of Ti segregation were reported in the surface of the V–Ti alloys [16]. To discuss the actual interfacial strength, it is needed to deal with a large-scale atomistic picture of the interface that includes misfit dislocations and microcracks. The small-size atomistic view described in this paper is a subset of such a large-scale view. If we could identify the structure or chemical composition at the interface, the small-size atomistic model could handle it as one of the variation of the actual interfaces. This understanding of the strength of the interface in the atomistic scale is essential in order to reduce trial and error processes by a systematic development of robust coating materials.

4. Summary

We have studied the bonding interface using a model that had three layers of CaO slab adhered to both sides of three layers of V slabs by means of the electronic structure calculation. We found that the relation of adhesive energy and separation distance of the interface is described well by the Rydberg function. The ideal strength of the interface was calculated to be 6.4 GPa. It is proposed that these methods could be applied towards systematic development of robust coating materials for fusion applications.

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