A Fundamental Study on Atomic Diffusion Phenomenon between Liquid Metal and Carbon Substrate

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In this study, atomic diffusion-ability of metals to glassy carbon and graphite is investigated by ab-initio molecular orbital calculation using AMOSS program and by a wetting experiment with the corresponding material systems in ultra-high vacuum. In the calculation, each of ethylene- and distorted ethylene-metal adatom is introduced as the atomic structural models of the glassy carbon and graphite systems respectively, and the molecular orbitals and total energies in the most stable bonding states are obtained by considering all possible states with ROHF method. Consequently, in the case of ethylene- or distorted ethylene-metal adatom model, corresponding to HOPG- or glassy carbon-liquid metal system in which mutual diffusion observes in the experiment, it is clear that carbon interatomic bonding is weakened by the formation of the occupied orbital due to the hybridization of the metal p-orbital and ethylene anti-bonding orbital.
Key words: wettability, mutual diffusion, liquid metal, carbon, ab-initio molecular orbital calculation

1. INTRODUCTION

Recently wetting phenomena of liquid metals on various kinds of carbon substrates become important to many carbon industrial applications. Pure carbon substrates are generally used for supporting high temperature liquid materials in order to manufacture metal wires, semiconductor products and polymer fibers. Among the wetting phenomena, atomic mutual diffusion is particularly the most important problem for carbon products. But wetting phenomena including atomic mutual diffusion have not been cleared theoretically and fundamentally as they have been treated empirically and experimentally in many industrial cases. If wetting phenomena are theoretically cleared and can be controlled, we are able to perform a lot of materials which have useful surfaces.

In this study, we intend to clear the wetting phenomena on several kinds of carbon substrates through experimental and theoretical approaches. As the experimental approach, we developed the original method for measuring contact angles on wires and plates.[1)2)] In this report, we introduce reliable data of contact angles and interaction energies between liquid metals and carbon substrates. In order to clear fundamental rules of chemical reaction corresponding to experimental wetting and atomic mutual diffusion phenomena, we investigate the electronic structure of interfaces between liquid metal and carbon substrate by ab-initio molecular orbital calculation program AMOSS. Model calculations are performed for the system of examination.

2. EXPERIMENT AND RESULTS

Fig.1 shows the schematic apparatus of wetting experiment in UHV (ultra-high vacuum) environment. Detail of the experimental method has been explained in previous papers.[1)2)] It is shown in it that the most important point in the experiment is to obtain a contamination-free contact of liquid and solid surfaces. Then the experiment must be done in the use of pure specimens under the clean conditions in UHV because the wetting phenomenon is based on the chemical bonds of the first-layer atoms of the surfaces. In order to confirm the wetting phenomenon of liquid metals on certain carbon surface structure, we use HOPG (Highly Oriented Pyrolyic Graphite) plate as a graphite single crystal substrate with (001) surface. Also, for comparing with the phenomenon on metastable carbon surface structure, we use glassy carbon plate which is thought to have mainly graphite micro crystal grain and partially diamond like sp_3 binding structure in grain boundaries. The other experimental method and conditions are same as written in previous papers.[1)2)]

Fig.2 shows configuration of liquid Cu on glassy carbon substrates. Cu thin film evaporated onto the glassy carbon substrate melts into liquid state by heating the substrate. Immediately the spread liquid copper changes into many micro sphere bolls by their own surface cohesive force. This phenomenon is caused by the reason that liquid copper has small interaction force with carbon substrate. In other cases of liquid noble metals, e.g. Au on HOPG,
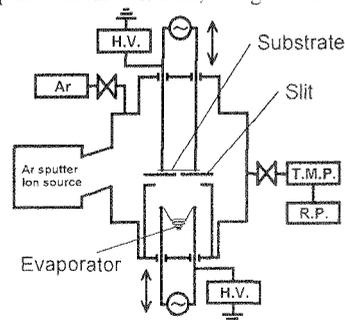
Fig.1 Schematic apparatus of wetting experiments.
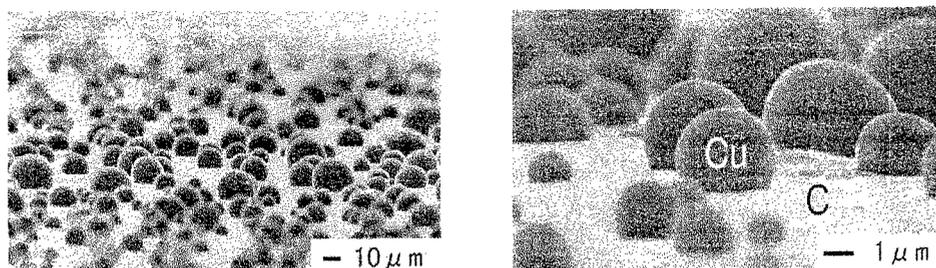
Fig.2 Configurations of liquid Cu on glassy carbon substrate.
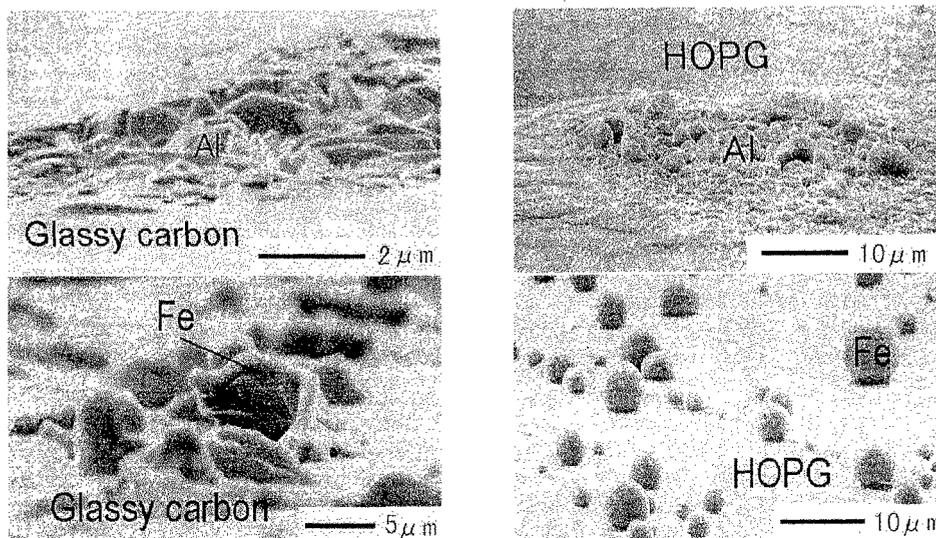
Fig.3 Configurations of atomic mutually diffused materials.

Table I   Averages of measured contact angles and estimated interaction energies.

Liquid metal	Glassy carbon		HOPG (001)	
	$\bar{\theta}$	γ_0 (J/m²)	$\bar{\theta}$	γ_0 (J/m²)
Au	126.0	0.470	125.4	0.480
Ag	111.5	0.572	116.3	0.503
Cu	119.8	0.646	118.1	0.679
Fe	Mutual diffusion		137.8	0.485
Al	Mutual diffusion		Mutual diffusion	

same configurations can be observed.

Fig.3 shows the atomic mutual diffusion when liquid Al and Fe is on the carbon substrate. Liquid Al mutually diffuses with both HOPG and glassy carbon substrates. Liquid Fe does only with glassy carbon substrate, not with HOPG substrate. When liquid Fe is on the HOPG substrate, it behaves same as liquid Cu, and hardly wet on the substrate comparing with liquid noble metals. This experimental result, that liquid Fe does not have chemical reactivity with HOPG (001) surface, is the most important of all, because liquid Fe has been generally thought to react easily or to have large atomic diffusion-ability. And this is grave news for carbon industries. We reveal the reason using the ab-initio molecular orbital calculation, and report in next section.

Averages of contact angles sampled in SEM images and estimated interaction energies using equation (1) ;

$$\gamma_0 = \gamma_l(1 + \cos\theta) \qquad (1)$$

are shown in Table I, where γ_l is surface tension of liquid metal and θ is contact angle. Values of surface tension are refereed from the table in "Metals Reference Book".[3]

In Table I, γ_0 means chemical binding strength between liquid metal atom and substrate atom, and we have understood it as "wettability" in a narrow sense. Mutual diffusion means that we can clearly observe alloy forming between liquid metal and substrate, and this should be the evidence of atomic mutual diffusion.

3. ESTIMATION OF WETTABILITY AND ATOMIC DIFFUSION ABILITY BY AMOSS CALCULATION

We have considered wetting phenomena by calculating interaction between liquid metal atom and substrate atom. In previous report,[2] we calculated binding energies and hybridized orbitals of two atom molecular model, and reached the conclusion that wettability is quantitatively determined by the binding energy of two atoms. The calculated result also showed mutual diffusion would occur in the cases that unpaired p- or d-electrons exist in both liquid metal and substrate.

In order to estimate wettability more quantitatively and to get further information of hybridization when mutual diffusion occurs, we perform cluster model calculations using ab-initio molecular orbital calculation program AMOSS. Restricted open-shell Hartree-Fock (ROHF) method is used to calculate energy levels. Cristiansen's

(a-1) Atomic configuration of diamond surface reaction   (a-2) Corresponding simple model of diamond surface reaction

(b-1) Atomic configuration of graphite surface reaction   (b-2) Corresponding simple model of graphite surface reaction
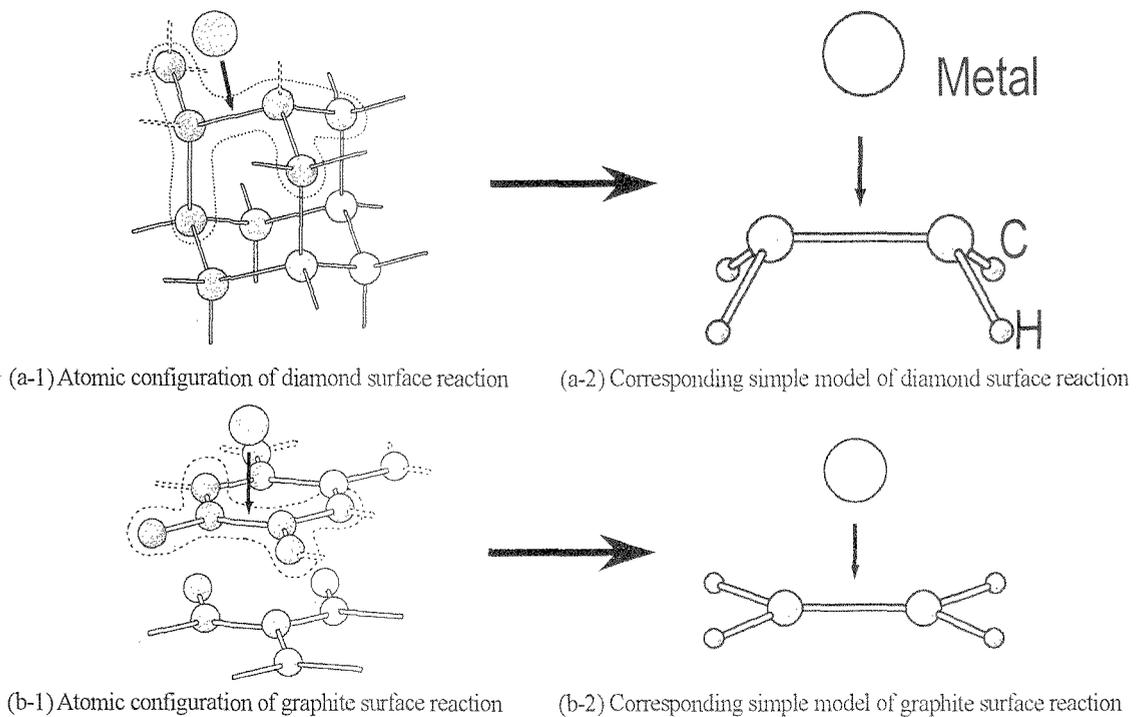
Fig.4 Atomic configurations of AMOSS calculation models. Left figures (a-1) (b-1) show actual surface reactions on diamond and graphite surfaces. Right figures show the simplest models which can explain frontier orbitals of inner-dot regions of left figures.

(a) Remarkable adiabatic potentials.   (b) Malliken population analysis of the lowest potential curves.
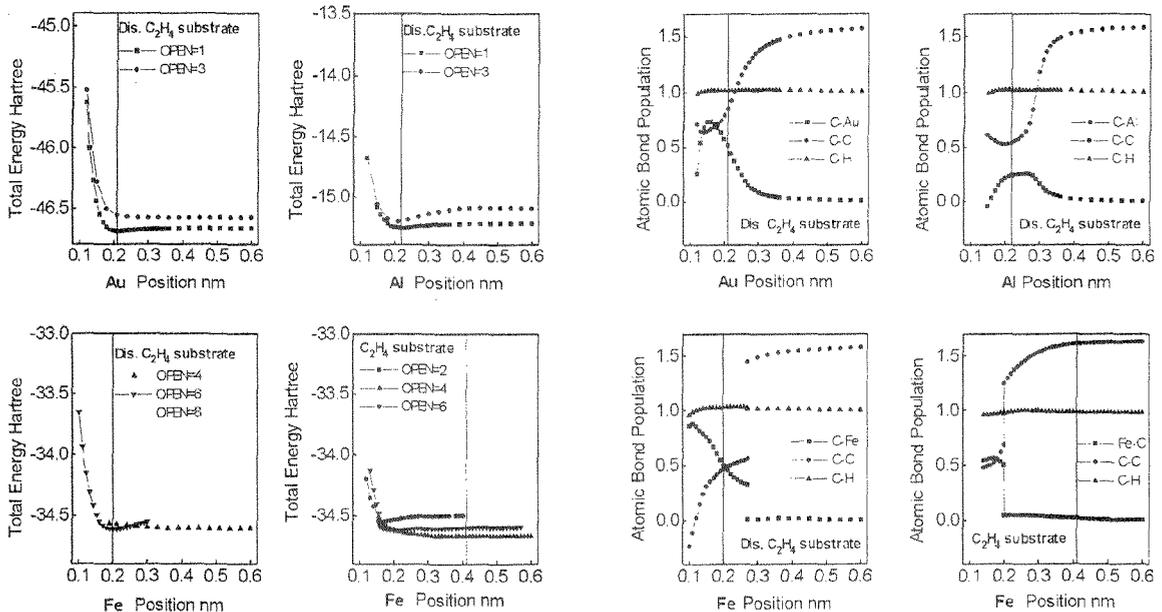
Fig.5 Calculation results. The vertical line in each figure means the position at the potential bottom of each case.

effective core potential[4] is used and electron correlation correction to energy is calculated using Moller-Plesset second-order perturbation (MP2) theory. The basis sets for each atom consist of the atomic orbitals that are the linear combinations of Gaussian functions. Only the Gaussian function of each orbital which has the lowest exponent is separated and used as the deferent basis for expressing accurately the spreading wave functions far from the atomic core. Mulliken population analysis is used to estimate binding strength between target atoms.

Table II   Calculated binding energies. Corresponding experimental interaction energy values are also shown as $\gamma_{\theta exp}$. M.D. means mutual diffusion.

Metal adatom	Dis.C_2H_4		C_2H_4	
	Binding Energy Hartree	G.C. $\gamma_{\theta exp}$ J/m^2	Binding Energy Hartree	HOPG $\gamma_{\theta exp}$ J/m^2
Au	0.0286	0.470	0.0140	0.480
Ag	0.0075	0.572	0.0063	0.503
Cu	0.0352	0.646	0.0136	0.679
Fe	0.0117	M.D.	0.0016	0.485
Al	0.0413	M.D.	0.0054	M.D.

Fig.4 shows the calculation models. When we use models constructed by many atoms, we waste a lot of CPU time and hardly analyze hybridization between target atoms. Then we adopt the simplest models which have fundamentally similar frontier orbitals to those of actual material surface. We check the frontier orbitals of these models by comparing with results calculated using large cluster models which give us results quantitatively agreeable with the physical values of original material surface. C_2H_4 model corresponds to a reaction between liquid metal and HOPG(001) surface. Dis.(Distorted)C_2H_4 model corresponds to a reaction between liquid metal and diamond structure which is contained in micro grain boundaries of glassy carbon. Although glassy carbon surface contains both C_2H_4 and Dis.C_2H_4 structure, chemical reaction is thought to begin at the Dis.C_2H_4 structure. Total energies are calculated approaching a liquid metal atom stepwise to a bond which connects carbon atoms of these models.

Calculated results are shown in Table II and Fig.5. As shown in Table II, the binding energies (B.E.) do not seem in good proportion to the experimental interaction energies. But comparing with calculated and experimental values on tungsten substrate introduced in previous papers,[1)2)] e.g. Au on W, calculated B.E.= 0.134 Hartree, experimental γ_θ= 2.20 J/m^2, binding energies qualitatively seems to be in good agreement with interaction energies. Then these calculation models are thought not to be large enough to get quantitative binding energy values.

Atomic diffusion ability is able to be explained using Fig.5. In the cases corresponding to mutual-diffusion experiment, Al on Dis.C2H4 and Fe on Dis.C2H4, atomic bond population between carbon atoms (C-C) clearly levels down when metal adatom is the potential bottom. In the cases corresponding non-mutual-diffusion experiment, atomic bond population is still high at potential bottom. Thus Al and Fe is thought to break the C-C bond easily and then to diffuse into grassy carbon substrate. These are also explained by configurations of frontier orbital hybridization. As seen in Fig.6 (b) and (c), Al and Fe p-orbital and C-C antibonding orbital hybridize together, and forms HOMO, thus C-C bond is weakened. In the other cases, C-C antibonding orbital does not hybridize with Au and Fe orbital and create HOMO, then C-C bond is not weakened. These orbital hybridization seem to dominate the experimental phenomena of atomic mutual diffusion. We think these simple idea is the fundamental low of atomic mutual diffusion, but in order to explain more actually, large model calculation analysis is going to be done.

-0.1162238D+00 No.12 (HOMO)   0.2637876D-01 No.13 (LUMO)

(a) Dis.C2H4-Au

-0.14851090+00 No.8 (HOMO)   0.384085D-01 No.9 (LUMO)

(b) Dis.C2H4-Al

-0.1389424D+00 No.13 (HOMO)   0.5916643D-01 No.14 (LUMO)

(c) Dis.C2H4-Fe

-0.3358192D+00 No.12(HOMO)   0.5094530D-01 No.13(LUMO)

(d) C2H4-Fe
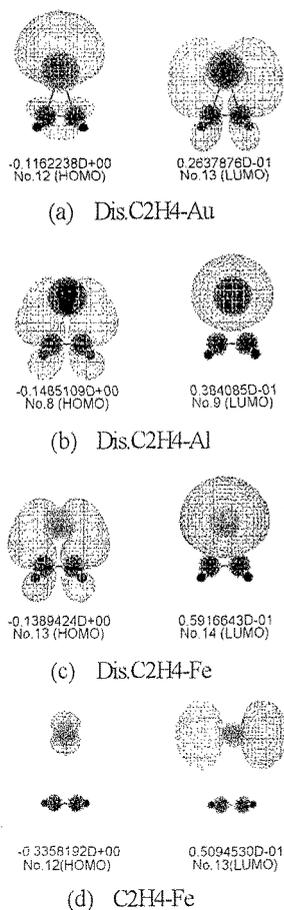
Fig.6 Remarkable configurations of hybridized wave functions of the most stable states at the adiabatic potential curves.

4. CONCLUSIONS

The contact angles of liquid metals on carbon substrates can be obtained. It is clearly found that liquid Fe does not diffuse into HOPG(001) surface but glassy carbon surface.

By calculating electron states of simple cluster models using AMOSS program, it is found that p-orbital of metal adatom hybridizes with C-C antibonding orbital of ethylene and forms HOMO in the cases of experimental atomic mutual diffusion. Thus it seems that atomic mutual diffusion ability is dominated by the hybridization between metal p- or d-orbital and antibonding orbital of substrate atoms and by their stabilization.

5. ACKNOWLEDGMENTS

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