AN ELECTRONIC APPROACH TO THE HYDROGEN OVERPOTENTIAL OF TRANSITION METALS AND ALLOYS

H. Ezaki, J. Saito and M. Morinaga
Toyohashi University of Technology
Toyohashi, Aichi 441, Japan

ABSTRACT

Hydrogen overpotential provides an important indication for the corrosion reaction of metals and alloys in aqueous solution, since it is a measure of the activity of the hydrogen evolution reaction on the metal surface. Such an electrochemical property has been suggested to correlate well with electronic structure, although any explicit explanation has not been given. In this study, the hydrogen overpotential of 3d transition metals and alloys was treated experimentally and also theoretically. The DV-Xα cluster method was employed in the calculation of electronic structures.

The trend of the hydrogen overpotential varying from metal to metal can be understood qualitatively from the bonding state of electrons in the metal near the Fermi energy level. Namely, if bonding-type intereactions are dominant, the metal shows a large overpotential, whereas if anti-bonding-type intereactions are dominant, the metal shows a small overpotential. The experimental data on the hydrogen overpotential of alloys can also be explained in a similar manner. The electronic structures were also simulated for metal and alloy surfaces where either a H atom or a proton or a H_2 molecule was adsorbed. Both the metal-hydrogen and the metal-metal intereactions were also shown to be important in understanding the hydrogen overpotential of transition metals and alloys.

INTRODUCTION

The hydrogen overpotential, which is a measure of the activity for the hydrogen evolution reaction on the metal surface, is one of the most important electrochemical properties. For example, hydrogen overpotential plays a dominant role in the corrosion of metals and alloys. In acidic solution, following two reactions occur simultaneously on the metal surface.

$$M \rightarrow M^{z+} + ze^- \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

Eq.(1) is the anodic dissolution reaction of metals. The metal M dissolves into the solution in the form of M^{z+} and remains z electrons on the metal surface. On the other hand, the H^+ ions existing in the solution discharge on the negatively charged metal surface and then hydrogen gas is evolved. The corrosion reaction proceeds at the rate which is determined from the above two reaction rates being in equilibrium.

The hydrogen evolution reaction expressed by eq.(2) is the total reaction, and several reaction steps have been proposed. The first step is the discharging of a proton onto metal surface. The discharged proton adsorbs on a metal surface as a hydrogen atom by following equation.

$$M + H^+ + e^- \rightarrow MH \tag{3}$$

The second step is the desorption of the adsorbed hydrogen atoms. Following two possible reaction paths have been proposed for this process.

$$2MH \rightarrow 2M + H_2 \tag{4}$$

$$MH + H^+ + e^- \rightarrow M + H_2 \tag{5}$$

The former reaction is the chemical desorption step without charge transfer, and this is well known as the Tafel step. The latter is known as the electrochemical desorption step. In this process protons discharge on the top of the adsorbed hydrogen atoms and then form H_2 molecules. A certain step among them becomes the rate-determining step for the hydrogen evolution reaction and this causes the overpotential of hydrogen evolution on the metal surface.

The trend of the hydrogen overpotential varies from metal to metal. Several attempts have been made to explain the characteristic of hydrogen overpotential of individual metals using various physical and/or electronic parameters. For example, they are the atomic number[1-3], the work function[2-4], the bond-strength of metals[5,6], the heat of adsorption of hydrogen on metals[7-9], and the electronegativity[10]. These previous results may suggest that the activity for the hydrogen evolution reaction is related closely to the electronic structures of metals, although any explicit explanation has not been given even for pure metals. Needless to say, the theoretical approach to the hydrogen overpotential is more difficult for alloys than pure metals.

In the present paper, the hydrogen overpotential for 3d transition metals and alloys was treated experimentally and theoretically. The electronic structure of metals and alloys were calculated by an advanced molecular orbital method. In addition, the metal and alloy surfaces where either a H atom or a proton or a H_2 molecule was adsorped, were simulated and their electronic structures were also calculated.

METHOD

Expeimental Procedures

The specimens of pure 3d elements except for Mn and of Fe-5mol%M (M; Ti, V, Cr, Mn, Co, Ni and Cu) were prepared by arc-melting. For these specimens, the hydrogen overpotential was evaluated by measuring cathodic polarization curves in a 1N sulfulic acid solution at 303K. A potentiostat was used for the polarization measurements.

Calculation of electronic structures

A discrete-variational(DV) Xα cluster method was employed in the calculation of electronic structures. This method is a molecular-orbital method in which the Slaters' Xα potential and the self-consistent charge approximation are used[11]. A detailed explanation of the calculation is given elsewhere[12,13].

The cluster model employed in the present calculation for 3d pure metals and alloys are shown in Fig.1(a) for hcp metals (Ti, Co), (b) for bcc metals (V, Cr, Fe), (c) for fcc metals (Ni, Cu) and (d) for Fe alloys. For Fe alloys, the central atom in the cluster shown in Fig.1(d) is replaced by various alloying elements M; M=Ti, V, Cr, Mn, Fe, Co, Ni and Cu. In this calculation, the overlap population which is a measure of the covalent interaction between atoms was obtained following the Mulliken population analysis.

Fig.2 shows the cluster model employed in the simulation of the hydrogen evolution on the metal and alloy surfaces. This cluster is constracted for the (001) plane of bcc Fe. It consists of nine atoms including an alloying element. In the first step, a hydrogen atom is adsorped on the top of the central atom (step 1). The adsorption position of the hydrogen atom in bcc Fe is not still known experimentally. In the present calculation our main interest is focused on the estimation of the alloying effects on the hydrogen evolution reaction on bcc Fe. For this purpose the hydrogen atom is positioned just on the top of the central atom

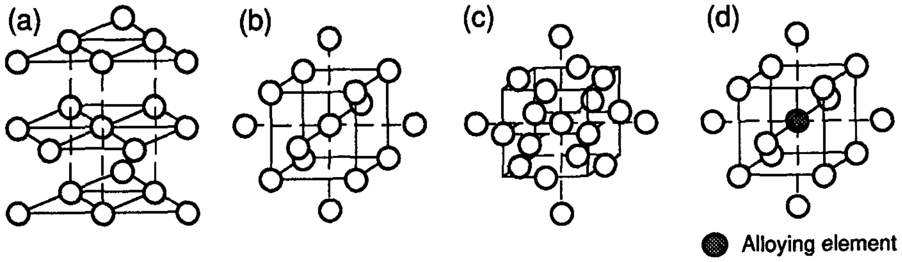

Fig.1 Cluster models of (a)hcp (Ti,Co), (b)bcc (V, Cr, Fe), (c)fcc (Ni, Cu) and (d) Fe alloy employed in the calculation of electronic structures.

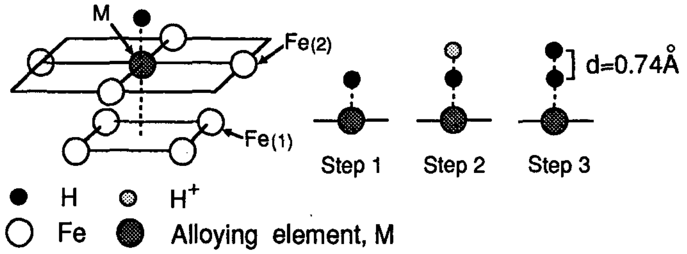

Fig.2 Cluster model of the (001) surface of bcc Fe and Fe alloys employed in the simulation for hydrogen evolution.

so that the adsorbed hydrogen atom interacts directly with the alloying element existing at the central atom position in the cluster. Also, such an atomic arrangement is convenient in the calculation because of the high symmetry of the cluster. However, the distance between Fe (or alloying elements) and adsorbed H atom is still ambiguous. So, the distance was changed in three steps, 1.50, 1.75 and 2.00Å by referring to the Fe-H interatomic distance in some iron-hydlides, and the optimum distance is determined in view of electronic bonding as presented below. Then a proton (step 2) and a H atom (step 3) are placed on the adsorped H atom at a distance of 0.74Å which correponds to the interatomic distance of a hydrogen molecule. Also, as described above, the central atom was replaced by the 3d element M and the above each step was simulated again. In this case, the distance between M and H atoms was corrected by the following equation.

$$d_{M-H} = 1.75\text{Å} + (R_M - R_{Fe}) \tag{6}$$

Here, 1.75Å is the optimum distance when the suface metal is pure Fe, and R_M and R_{Fe} are the metallic radius of M and Fe, respectively. Thus, the M-H distance was varied by taking account of the metallic radius of M.

RESULTS AND DISCUSSION

Hydrogen overpotential for metals and Fe alloys

Fig.3 shows the results of the measured hydrogen overpotential for pure metals at the cathodic current density of 10mA/cm^2. Among these 3d elements, Ti shows the largest hydrogen overpotential. As the atomic number increases, the hydrogen overpotential becomes lower and reaches a minimum at Ni, and then again increases at Cu. Such a trend is consistent with the results reported in previous study[2,3].

The results of the hydrogen overpotential for Fe alloys are presented in Fig.4. Interestingly, the hydrogen overpotential is almost similar among the alloys containing Ti, V, Cr, Mn and Fe. In contrast to this, for the alloys containing Co, Ni and Cu, there are large changes in the hydrogen overpotential. The trend of its change quite resembles that of pure metals, Co, Ni, and Cu, as is seen by comparing Fig.3 with Fig.4. These results suggest that the addition of the left side elements of base metal Fe in periodic table does not change the hydrogen overpotential of Fe alloys. On the other hand, when the right side element is alloyed, the hydrogen overpotential changes largely with the alloying element. In this case, the characteristic hydrogen overpotential of the alloying element reflects in the hydrogen overpotential of Fe alloy.

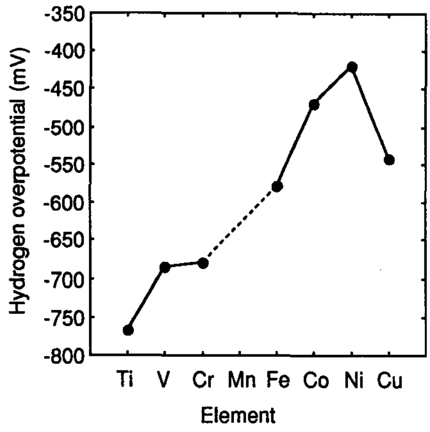

Fig.3 Hydrogen overpotential for 3d transition metals at the current density of 10mA/cm^2.

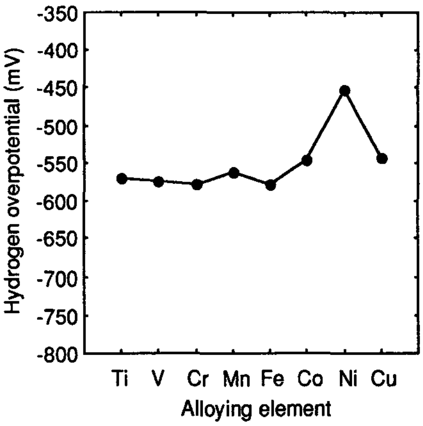

Fig.4 Hydrogen overpotential for Fe alloys at the current density of 10mA/cm^2.

Hydrogen overpotential and electronic states of metals and alloys

As easily found from eqs. of (2), (3) and (5), the electron transference is necessary to occur the hydrogen evolution reaction. In addition, transferred electrons should be taken away from the metal surface as a result of evolution of hydrogen gas. In view of these facts, it can be presumed that the bonding state of electrons in metal will correlate well with the activity for the hydrogen evolution reaction of each metal. Also, this presumption is supported by the fact that the hydrogen overpotential changes with elements, following the position in periodic table.

In Fig.5, the energy distribution of the overlap populations of d electrons is shown for pure 3d metals. In this figure, each energy distribution is drawn by setting each Fermi energy level, Ef, to be zoro. This overlap population is a measure of the strength of the covalent bonding between atoms. If the overlap population is positive(+), bonding-type interactions are operating between atoms, whereas if it is negative(-), antibonding-type interactions are dominant between atoms. As shown in this figure, the Ef level of Ti is located well below the energy where the interactions change from bonding to antibonding. In other wards, the d electrons contribute to the bonding between Ti atoms. These bonding-type electrons near Ef are probably associated with the hydrogen evolution reaction. Such electrons are strongly bound and the use of them for the hydrogen evolution reaction is not preferable in view of the chemical bond nature. Therefore, the electronic bonding state in Ti will put a barrier to the hydrogen evolution reaction, and this may cause the large hydrogen overpotential in Ti. Even if the extra electrons are moved into Ti from the electronic circuit, the situation is supposed to be unchanged, because the Ef level may not change largely. The energy region where the bonding-type interactions are operating is filled gardually with electrons as the atomic number of metals increases, and fully filled at Cr.

In contrast to this, the Ef levels of Fe, Co and Ni locate at the energy regions where the antibonding-type interactions are dominant. For these metals, electrons near Ef do not contribute to the bonding between metal atoms. If hydrogen evolution reaction occurs on these metal surfaces, the antibonding-type electrons near Ef are probably associated with this reaction. This is favorable in view of the chemical bond nature. Namely, it can be said that these metals have a tendency to promote the hydrogen evolution reaction in view of the bonding state of electrons. The overlap populations of antibonding-type electrons, which are represented by the area of the negative region until Ef, increases in the order, Fe, Co, Ni. In response to this change, the measured hydrogen overpotential of these metals continue to decrease as shown in Fig.3. For Cu, the Ef locates well higher energy region of d-band and its d-orbitals are completely filled with electrons. Namely, d-electrons will be no longer responsible for the hydrogen evolution reaction in Cu. Such a difference in the electronic state may cause the hydrogen overpotential drop at Cu as shown in Fig.3.

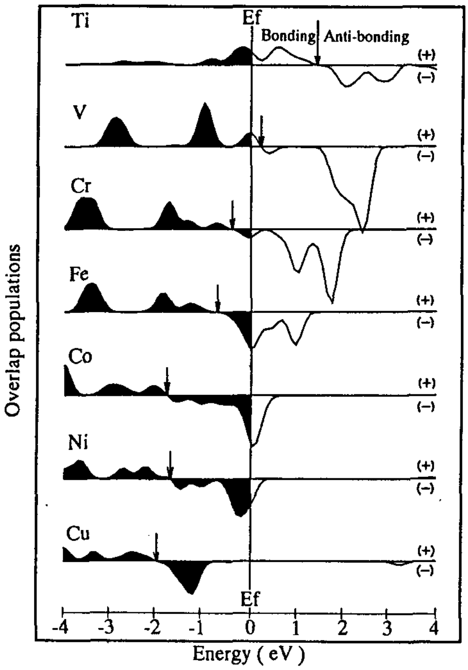

Fig.5 Energy distributions of the overlap populations of d electrons for 3d transition metals.

In addition to the trend for the electron transference discussed above, metal-hydrogen interactions are also important in understanding the hydrogen overpotential as might be expected from the reaction step of eq.(3) and (4). In previous study, several electronic approaches has been carried out to the problem of hydrogen in metals[14-16] because of its practical importance in understanding the hydrogen embrittlement or the hydrogen storage of metals. When the hydrogen atom is absorbed into metals, the Fermi energy level of the metal has been known to be raised up[16]. In the case of Ti, the raising of the Ef results in the increase of d-d interaction as is easily found from the overlap population shown in Fig.5. Therefore, absorption of more hydrogen atoms is so effective in strengthening the atomic bond in Ti. As to the hydrogen evolution reaction, the discharged protons will be trapped strongly into Ti, and this becomes a barrier to the following desorption step presented by eq.(3) and (4). The large hydrogen overpotential of Ti can also be explained from the above standpoint.

On the other hand, the raising of the Ef increases apparently antibonding-type electrons in metals whose Ef is located at the energy region where the antibonding-type interactions are operating. This causes the decrease in the d-d bond strength between metal atoms. Therefore, active absoption of hydrogen atom is not preferable in these metals in view of the electronic bonding. Consequently, these metals tend to desorb the hydrogen atoms rather than to absorb them. In addition to the easiness of electron transference in these metals, such a tendency of hydrogen desorption will make their hydrogen overpotential very small.

Hydrogen overpotential and electronic states of Fe alloys

Fig.6 shows the energy distributions of the overlap populations for Fe-M alloys. Each distribution in the figure is concerned with the d-d interactions between Fe and M atoms. It is interesting to note that the local electronic states of M in Fe is quite different from those of M in pure M. For example, the Ef of Fe-Ti cluster locates at the energy region

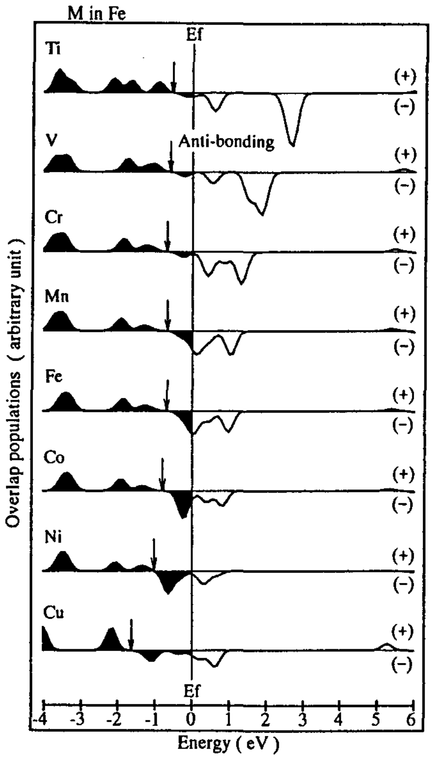

Fig.6 Energy distributions of the overlap populations of d electrons for Fe alloys.

where the antibonding-type interactions are operating, whereas the Ef of pure Ti locates at the energy region where the bonding-type interactions are operating. It can be seen that all of the Ef's of Fe-M alloys locate at the antibonding energy region, and its energy region up to the Ef extends further with increasing atomic number of alloying element M. Thus, so far as the electronic bonding state is concerned, the activity for the hydrogen evolution reaction will be expected to increase in the same order. In Fe alloys, however, it should be considered that two regions co-exist on the surface. One is the Fe matrix region and another is the alloying-element containing region. Compared to the local electronic states of Fe-Ti, -V, -Cr and -Mn, it is found that the local electronic state of Fe is more favorable for the hydrogen evolution reaction. As a result, hydrogen evolution reactions will occur at the Fe-matrix rather than the alloying-element containing region. On the other hand, local electronic states of Fe is found to be less favorable compared to those of Fe-Co, -Ni and -Cu. In this case, hydrogen evolution reaction will occur at the alloying-element containing region. Consequently, the hydrogen overpotential for Fe alloys exhibits a similar tendency to that for pure elements, as is shown in Fig.4. Such an electronic states consideration can explain the variation in the hydrogen overpotential for Fe alloys consistently.

Electronic strucrural change due to the hydrogen evolution reaction

In the above section, the hydrogen overpotential of metals and alloys has been treated in view of their local electronic states. In this section, the electronic structural change are examined by simulating the hydrogen evolution reactions on metal and alloy surfaces. The following three steps were simulated of the hydrogen evolution reaction. Step 1 is the adsorption of an H atom to the metal surface and this corresponds to the Volmer step of eq.(3). Step 2 is the discharging of the proton on the adsorbed H atom. This step corresponds to the electrochemical desorption step of eq.(5). Step 3 is the formation of the stable hydrogen molecule.

Interatomic distance between Fe and H atoms

In this simulation, it is important to know the distance between

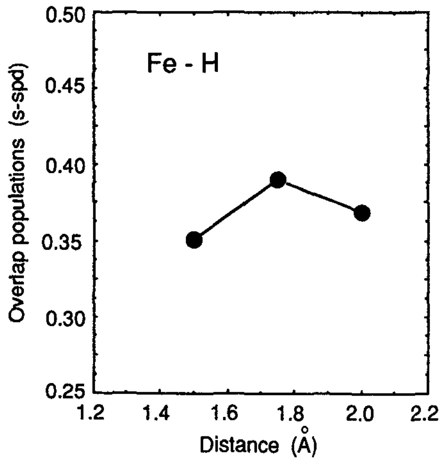

Fig.7 Change in the overlap populations between the adsorbed H atom and the Fe atom with the distance between them.

surface metal atom and adsorbed hydrogen atom. So, in this calculation the effect of the interatomic distance on the electronic structures was examined first using the cluster model for step 1 shown in Fig.2. Fig.7 is the result for the overlap population which is a measure of the covalent bonding between H and Fe atoms. As is evident from this figure, the overlap populations show a maximum when the H atom is adsorbed at the distance of 1.75Å. This distance of about 1.75Å will be supposed to be most likely for the adsorption distance between H and Fe atoms. Therefore, the distance of 1.75Å is employed in the following calculations.

Charge transfer and atomic interactions between Fe and H atoms

Fig.8 shows the ionicity of H atoms in each reaction step calculated for pure Fe surface. Here, the ionicity is presented only for the first-nearest H atom from the central Fe atom. As shown in Fig.8, the ionicity of adsorbed H atom in step 1 has a relatively large value with the negative sign. This indicates that electron transfer takes place from Fe atoms to the adsorbed H atom. In contrast to this, the ionicity of the H atom in step 2 is close to the neutral. This indicates that the electron transfer between Fe and adsorbed H atom is reduced suddenly if a proton adheres to the adsorbed H atom. A similar value of the ionicity is obtained in step 3, in which an H_2 molecule exists stably on the surface. It is likely that the stable hydrogen bonding is already formed between an adsorbed H atom and a proton even in step 2.

The interactions between Fe and H atoms are also variable, depending on the step. For example, Fig.9 shows the overlap populations between Fe and the nearest H atom in each step. Compared to the strong interaction in step 1, there is the weak interaction in step 2 and in step 3.

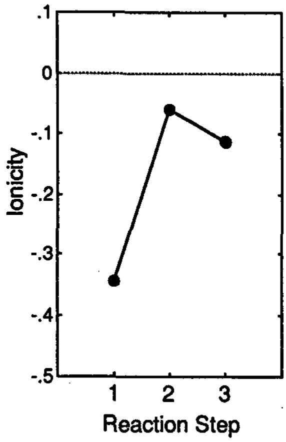

Fig.8 Ionicity of the H atom adsorbing the on the top of the central Fe atom for each reaction step.

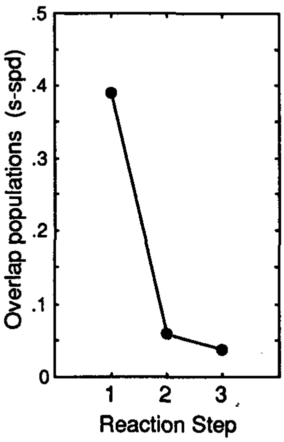

Fig.9 Overlap populations between Fe atoms and the H atom adsorbing on the top of the central Fe atom for each reaction step.

Charge transfer between metals due to the hydrogen evolution

The charge transfer also takes place between metal atoms as a result of electron transfer to the H atom. The ionicities of M, Fe(1) and Fe(2) atoms in each step are shown in Fig.10(a) for pure Fe, (b) for Fe-M(Ti) and (c)

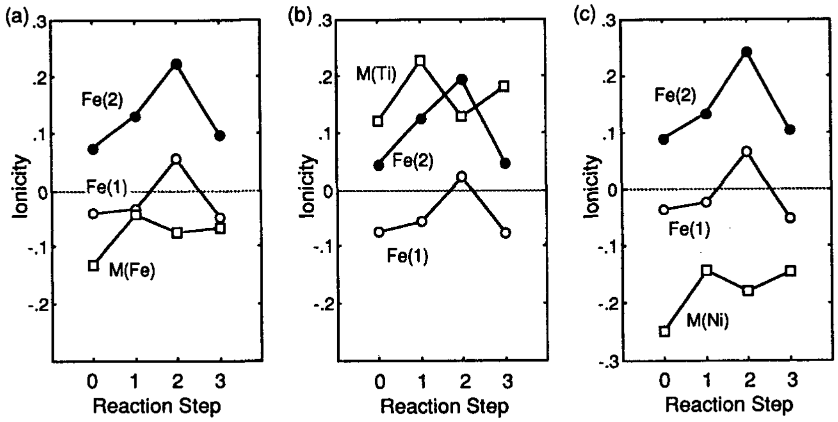

Fig.10 Ionicities of metal atoms in (a)pure Fe, (b)Fe-Ti and (c)Fe-Ni for each reaction step.

for Fe-M(Ni). Here, M is the central atom, Fe(1) is the first-nearest neighbor Fe atom, and Fe(2) is the second-nearest neighbor Fe atom from the central M atom as shown in Fig.2. The first- and second-nearest-neighbor Fe atom corresponds to 4 Fe atoms on the lower layer and 4 Fe atoms on the upper layer, respectively. Furthermore, the notation of Step 0 in these figures means the initial state with no hydrogen atom adsorbing on the surface.

Here, attention is focused on the ionicity change of each atom in pure Fe shown in Fig.10(a). By comparing step 0 with step 1, it is apparent that each ionicity of M(Fe) and Fe(2) changes largely and shifts towards the positive direction in step 1, whereas there is the less change in the ionicity of Fe(1). Such ionicity changes indicate that the transferred electrons to the H atom are mainly provided from the central atom and the surface Fe(2) atoms in step 1. In the case of step 2, each ionicity of Fe(1) and Fe(2) atoms becomes more positive while that of the central Fe atom is less-changed or becomes slightly negative compared to the ionicity in step 1. Namely, in step 2, electrons are provided from not only the surface Fe atoms but also the lower layer Fe atoms. In this case, the central atom acts mainly as the electron path without providing electrons to the H atom. In step 3, the ionicity of each atom returns approximately to the value of the initial state (step 0) because the adsorbed hydrogen atoms form a stable H_2 molecule in this step, and the molecule does not interact strongly with the surface metal atoms, but only the weak interaction is still remains with the central Fe atom.

A similar ionicity change in each step can also be seen in Fe-M(Ti) and Fe-M(Ni) alloys as shown in Fig.10(b) and (c). The ionicity of M atoms changes remarkably, but its change simply follows the electronegativity. The elctronegative Ni has a negative ionicity and the electropositive Ti has a positive ionicity. Fe has an intermediate ionicity between them.

There have been no previous reports on the charge transfer in metal atoms induced by the hydrogen evolution reaction. This is the first calculation of revealing the intersting charge transfer behavior near the metal surface.

Change in the bond strength of metals and alloys with hydrogen evolution

In a previous section, it was mentioned that the absorption of H atoms into metal varies the d-d bonding between metal atoms in Fe. Fig.11 shows the overlap populations between M and Fe atoms for each step. It can be seen from this figure that the overlap populations between M and Fe atoms in step 0 decreased apparently by the adsorption of H atom (step 1) in pure Fe i.e. Fe-Fe, Fe-Co, Fe-Ni and Fe-Cu, as was expected from the local electronic state consideration described before. Therefore, the regions containing such alloying elements will have a tendency to desorb the H atom in order to recover the original metal bonding. This is in good agreement with the experimental result that the hydrogen overpotential which is characteristic of each alloying elements, reflects in the measured hydrogen overpotential of Fe alloys containing Co, Ni and Cu.

On the other hand, for Fe-Ti, Fe-V, Fe-Cr and Fe-Mn alloys, the overlap populations are higher in step 1 than in step 0. This is also consistent with the discussion described before.

The lower overlap populations in step 2 than in step 1 means that there is still M-H interaction remaining to some extent in step 2. However, such an interaction becomes weaker in step 3, resulting in the increase of the overlap populations between M and Fe atoms.

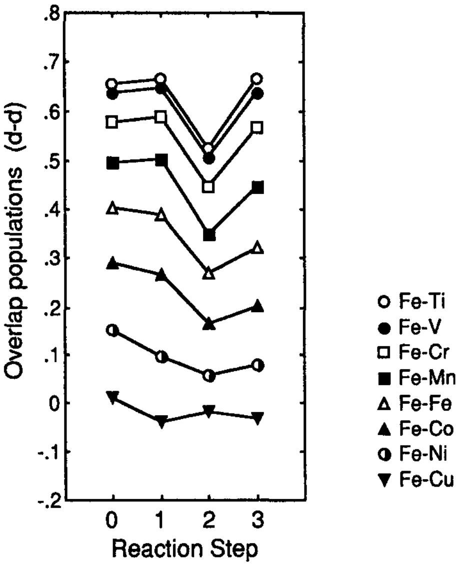

Fig.11 Overlap populations between metal atoms for each reaction step.

<u>M-H interactions</u>

As already mentioned, the strong bonding between metal and H atoms will tend to prevent the desorption of H atom from the metal surface in hydrogen evolution reaction. Thus the magnitude of the M-H interaction is also important in understanding the hydrogen overpotential. Fig.12 shows the overlap populations between alloying element M and adsorbed H atom calculated for step 1. The left side elements of Fe in periodic table, Ti V, Cr and Mn, have a stronger interaction with the H atom compared to that of Fe, while the right side elements, Co, Ni and Cu have a weaker interaction. In Fe alloys containing the former elements, H atoms will be adsorbed strongly in the alloying-element containing region rather than in the Fe-matrix region. As the result, the Fe-matrix becomes preferalbe sites for the hydrogen evolution reaction in these alloys. By contraries for Fe alloys containing the latter elements, the alloying-element containing region becomes preferable sites rather than the Fe-matrix region. The experimental results on the hydrogen overpotential for Fe alloys can also be understood consistently from the above standpoint of M-H interactions.

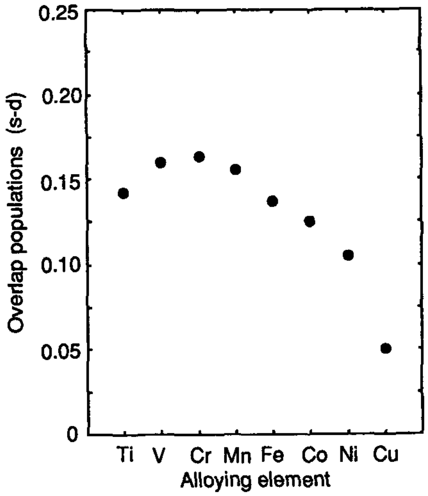

Fig.12 Change in the overlap populations between M atom and adsorbed H atom with alloying elements.

CONCLUSIONS

In the present study, the hydrogen overpotential for 3d transition metals and Fe alloys containing 3d elements were first examined experimentally. The hydrogen overpotential for pure metals decreased with increasing atomic number of metals and it becomes minimum at Ni. For Fe alloys, the hydrogen overpotential changes when the right side elements of Fe in periodic table are alloyed into Fe. In this case the hydrogen overpotential of alloys reveals the characteristics of the hydrogen overpotential of the alloying elements.

Such a variation in the hydrogen overpotential for transition-metals and alloys can be explained consistently by considering the electronic states of metals and alloys. In particular, the bonding states of electrons are primarily important. It is shown from the simulation of the hydrogen evolution on metal and alloy surfaces that both the metal-metal interaction and the metal-H interaction are important in understanding the hydrogen overpotential of metals and alloys.

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